THE SERPENTINIZED ULTRAMAFITES OF THE SHETLAND CALEDONIDES

VOLUME I. TEXT.

Thesis submitted in accordance with the requirements
of the University of Liverpool for the degree
Doctor of Philosophy by David Thomas Moffat

1987

Abstract

The Serpentinized Ultramafites of the Shetland Caledonides

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Ultramafites, as in many other orogenic terrains, are widespread within the Shetland Caledonides. The ultramafites form nearly a hundred separate units, comprise many different lithologies and occur in a wide variety of structural and petrological associations. Unfortunately, tectonism and metamorphism makes direct interpretation of the origin of many of the ultramafites extremely difficult. Not least because the criteria for discrimination between origins are not well established for ultramafites within orogenic terrains in general. Consequently, some objective means of defining the tectonomagmatic affinity of ultramafites within orogenic terrains would be invaluable. Having identified the tectonomagmatic affinity of an ultramafite it would be possible to then theorise as to its regional significance and importance as a marker of fundamental tectonic lineaments within the orogen.

The research thesis: (a) describes the geology of the ultramafites within the Shetland Caledonides; (b) investigates the application of REE discrimination techniques to ultramafites, and (c) tests and applies the REE discrimination techniques on selected Shetland ultramafites.

The serpentinized ultramafites of the Shetland Caledonides are considered under two main groupings: (a) ultramafites within tectonostratigraphic/metamorphic units, and (b) ultramafites within calc-alkaline plutonic complexes. The first group comprises ultramafites involved in orogenesis either at a secondary level as part of the pre-orogenic continental lithosphere (eg. Archean Lewisian inliers) or as an intrinsic part of the orogens development. The latter includes, most notably, the Dunrossness spilite group, identified as a ca. 590 Ma magmatic sequence developed as the culmination of a major basin-deepening sequence within the Dalradian-like succession. The Shetland ophiolite is a ca. 470 Ma, supra-subduction zone complex developed in a probable marginal-basin setting after the Grampian orogenic phase of the Scottish and Shetland Caledonides. Ultramafites within calc-alkaline plutonic complexes are similar to Appinite-type complexes in the British Caledonides and elsewhere (eg. Klamath Mts., California).

Four ultramafite REE discrimination methods are presented: (a) a summary table, which allows qualitative comparison between ultramafites; (b) Ce_N v Yb_N discrimination diagram; (c) Ce_N/Sm_N v Sm_N/Yb_N discrimination diagram; (d) multiparameter-condition tree, where key REE profile parameters (Ce_N, Sm_N Yb_N Ce_N/Yb_N, Ce_N/Sm_N, Sm_N/Yb_N, profile shape) and fractionating conditions are arranged sequentially in a tree-like structure. Ultramafites in the discrimination methods are considered in nine tectonomagmatic groups:

Ophiolites, Alpine-type complexes, Oceanic peridotites, Layered complexes, Appinite-type complexes, Continental picrites, Oceanic picrites, Boninites and Peridotitic komatiites. Each discrimination method has discriminant attributes not shown by the others. Compounding the discrimination results from all three diagramatic ultramafite REE discrimination methods identifies the tectonomagmatic affinity of an ultramafite under investigation. Serpentinization does not usually affect ultramafite REE discrimination. However, REE mobility and fractionation during advanced metasomatic alteration (steatitization) is complex and variable for the systems studied and can significantly influence ultramafite REE discrimination.

Acknowledgements

Many people have helped during the preparation of this thesis. The author would like to express his special thanks to Professor D. Flinn (Liverpool) for his guidance, helpful advice during the course of the research, and for critically reading the text. Drs. A.L. Harris, S.J. Buttler, T. Robinson, and other colleagues and friends in the Department of Geological Sciences, University of Liverpool provided valuable discussion on various aspects of the research project. I should also like to thank Professor R.W. Nesbitt (Southampton) for specific advice and discussion on the petrography of ultramafites from the Dunrossness spilite group, S Shetland.

XRF analytical facilities were made available by Dr M.P. Atherton (Liverpool); ^{40}Ar/^{39}Ar radiometeric dating facilities were made available by Dr A. Mussett (Liverpool). Thanks go to M.S. Brotherton (Liverpool), along with the staff at the University's Research Centre, Risley, for assistance and advice on the use of the RNAA facilities. I should like to thank D. Plant and T. Hopkins at the Department of Geology, Manchester University for the use of electron microprobe facilities.

The research work was carried out with grant support from the University of Liverpool (University postgraduate studentship) and Imperial Chemical Industries (ICI Educational Trust postgraduate studentship).

I should like to thank Sue Beetlestone, who typed the text and Viv Jenkins who typed the figure captions.

The writing of a text such as this makes significant inroads into one's spare time and calls for considerable patience from one's family. My wife and parents have been immeasurably tolerant during the past few years and have been a great source of help in every way possible.

CONTENTS VOLUME I

Page No.

Page No

CONTENTS VOLUME II

List of Figures

Page No

Page No

List of Tables

List of Appendices

1 Introduction

1.1 Aims of research

1.1.1 Background to research problem

Ultramafites, as in many other orogenic terrains, are widespread within the Shetland Caledonides. the ultramafites form nearly a hundred separate ultramafic units, comprise many different rock types and occur in a variety of field and petrological associations. Many consist of small isolated tectonic blocks, others occur in close spatial association with gabbros, dolerites and pillow basalts, elsewhere they occur as major massifs covering many square kilometres. We may expect, therefore, that there are a variety of origins and emplacement histories for the ultramafites. Unfortunately, tectonism and metamorphism makes direct interpretation of the origin of many of the ultramafites in the Shetland Caledonides extremely difficult. Not least because the criteria for discrimination between origins are not, as yet, well established or at least broadly accepted for ultramafites within orogenic terrains in general.

Thayer (1960) was the first to make a clear distinction between peridotites in layered complexes, whose cumulate structure and texture are of magmatic origin, and what he termed Alpine-type complexes, whose tectonic structure and textures are indicative of solid-state flow. The Alpine-type complexes, which comprise those bodies emplaced in orogenic belts, were further divided into two sub types by Den Tex (1969) depending on whether the peridotites are parts of ophiolite complexes (Ophiolitic peridotites) or peridotites incorporated in 'root zones' of orogenic belts. The latter roughly equated with the 'high temperature' peridotites of Green (1967). Jackson and Thayer (1972) divided the Alpine-type (or orogenic peridotites) using petrographical and geochemical criteria, into lherzolitic and harzburgitic subtypes. Chidester and Cady (1972) divided the Alpine-type peridotites into allochthonous sheetlike, intrusive or diapiric and exotic bodies. Nicolas and Jackson (1972) combined the Den Tex (1969) and Jackson and Thayer (1972) divisions, showing that the 'root zone' peridotites are generally lherzolitic and the Ophiolitic peridotites, harzburgitic. They argued that the lherzolite massifs, abundant in the western Mediterranean represent sub-continental upper mantle emplaced into the continental crust. The harzburgites, represent the uppermost oceanic mantle tectonically emplaced at a high level onto the continental crust; the mantle sequence and overlying oceanic crust is then equated with an ophiolite section. The differences in mineralogical and geochemical composition between the lherzolitic and harzburgitic massifs they attributed to the harzburgites having been through a partial melting and depletion history at a constructive plate margin. Other smaller ultramafic bodies in high-grade metamorphic terrains were regarded as having been emplaced in a similar fashion to the lherzolites and harzburgites during an older orogenic phase and later deformed and metamorphosed. The Ophiolitic peridotites and Ophiolite assemblages were more rigorously defined in Anon. (1972). Coleman (1977) demonstrated that Ophiolitic peridotites are exposed along belts of intense tectonism and generally mark the sites of earlier interactions between oceanic and continental lithospheres (geosutures).

Taylor and Noble (1960) recognised a third type of ultramafic body within orogenic terrains, the Alaskan-type or concentric-zoned ultramafic complex. These bodies have been identified in a number of orogenic belts and have features which clearly distinguish them from Alpine-type ultramafic massifs (Irvine, 1967, 1974; Taylor, 1967). The Alaskan-type complexes commonly appear to have undergone diapiric/plutonic emplacement after primary differentiation. The ultramafic rocks are arranged in a crude zonal pattern, with a cumulate dunite core surrounded by successive shells of peridotite, olivine pyroxenite, magnetite and hornblende pyroxenites (Irvine, 1974 and 1976).

More recently other types of ultramafic and related rock associations have been described from orogenic terrains. For example, peridotitic komatiites have a widespread distribution in Archean 'greenstone' belts and some post-Archean orogenic belts (*cf.* Arndt and Nisbet, 1982). In addition, layered complexes, originally thought to be essentially non-orogenic, have been identified in a syn-orogenic setting (e.g. Wilson, 1981; Bennett and Gibb, 1983). It is therefore clear that any simple two-fold division of the ultramafites within orogenic terrains into Ophiolite (harzburgitic) and Alpine-type (lherzolitic) complexes is of limited usefulness. Such a division does not accommodate the possibility that many other types of ultramafite may be involved in orogenesis, either at a secondary level as part of the pre-orogenic continental lithosphere or as an intrinsic part of an orogens development. It is conceivable, therefore, that a wide variety of ultramafites may potentially occur in orogenic terrains. These include the following, generally accepted, ultramafite groups: Ophiolite complexes, Alpine-type complexes, Oceanic peridotites, Layered complexes, Appinite-type complexes, Alaskan-type complexes, Continental picrites, Oceanic picrites, Boninites, Peridotitic Komatiites, Kimberlites and Alkaline ultramafic complexes.

N.B. The ultramafite groups listed above provides only a working classification and framework for discussion to be modified as we learn more about the petrogenesis of the ultramafites. There may also be a degree of overlap between rocks of two or more groups and between groups themselves.

It is clear that many of these ultramafite groups represent widely differing tectonomagmatic environments, yet under tectonic and sedimentary reworking during orogenesis they may be rendered indistinguishable in the field. Frequently ultramafites within orogenic terrains are completely altered to secondary assemblages and original structural relations hidden by later tectonism. Consequently, some objective means of discriminating between possible ultramafite group alternatives would be invaluable in the study of ultramafites within orogenic terrains. Thus having identified the tectonomagmatic affinity of an ultramafite it would be possible to go on and theorise as to its regional significance and importance as a marker of fundamental tectonic lineaments.

1.1.2 Statement of purpose

In the light of the above discussion the main objectives of the research concerning the serpentinized ultramafites of the Shetland Caledonides are three fold:

(a) to describe the geology of the ultramafites of the Shetland Caledonides;

(b) to investigate the application of REE discrimination techniques to ultramafites of differing tectonomagmatic affinity, and

(c) to test and apply useful REE discrimination techniques on selected Shetland ultramafites.

1.1.3 Limitations of research

The research study is limited specifically to variously serpentinized ultramafites (altered peridotitic and pyroxenitic protoliths), rather than hornblendic ultramafites which are also numerous throughout Shetland.

1.1.4 Scope of coverage

The text is organised in five major sections.

The aims of section 1 (**Introduction**), in addition to a statement on the purpose, definition, background description and limitations of the research (see above), are:

(a) to give a clear description of the geographical location of the research area and spatial distribution of ultramafites in the Shetland Caledonides;

(b) to provide expanded and sentence definitions of terms used in petrological descriptions and petrogenetic discussions

(c) to review earlier research and identify relevant information sources on Shetland ultramafites, and

(d) to detail field and geochemical analytical techniques employed in the research.

The aims of section 2 (**Ultramafites within tectonostratigraphic units of the Shetland Caledonides**) are:

(a) to summarize the geological setting and age relations of ultramafites within various metamorphic units of the Shetland Caledonides;

(b) to detail field, petrological and geochemical characteristics of the ultramafites;

(c) to discuss possible mechanisms of ultramafite emplacement and petrogenesis;

(d) to comment on the possible correlation of ultramafites within the Shetland Caledonides, and

(e) to determine, or in the case of the Shetland ophiolite to confirm, the geological provenance and tectonomagmatic affinity of the ultramafites.

The aims of section 3 (**Ultramafites within calc-alkaline plutonic complexes of the Shetland Caledonides**) are:

(a) to present a review of the occurrence, age relations, petrology and geochemistry of ultramafites associated with calc-alkaline plutonic complexes in Shetland;

(b) to establish, primarily from the internal structure and petrography of the ultramafites, their mechanism of emplacement;

(c) to investigate the petrogenesis of the ultramafites, and

(d) to test the petrological consanguinity of the ultramafites and other units of the relevant plutonic complex.

The aims of section 4 (**REE discrimination of Shetland ultramafites**) are:

(a) to review the REE geochemistry of ultramafites which may occur in orogenic terrains

(b) to identify from the data any similarities (or differences) which may exist between ultramafites

(c) to asses the affects of REE mobility and fractionation during alteration processes on ultramafites

(d) to devise means of discriminating between ultramafites of differing tectonomagmatic affinity using REE, and

(e) to apply the possible REE discrimination methods to selected ultramafites from the Shetland Caledonides.

The aims of section 5 (**Summary and conclusions**) are:

(a) to summarize the geological data and conclusions on Shetland ultramafites given in sections 2 and 3 of the main body of the thesis;

(b) to provide a comprehensive overall interpretation of the ultramafites within the Shetland Caledonides

(c) to reinforce, interpret and otherwise clarify the application of REE discrimination methods to Shetland ultramafites given in section 4, and

(d) to summarize, appraise and make recommendations on the general application of the ultramafite REE discrimination methods described in section 4.

1.2. Geographical location of research area.

The Shetland Isles lie about 165 km NE of the Scottish mainland and about 340 km W of Bergen in Norway (see Figure 1.2-1a), between latitude 59°50' - 60°50' and longitude 0°40' - 1°40'W. The archipeligo extends for some 110 km from north to south and consists of well over a hundred islands, of varying size, which give a total land area of about 1440 km^2 and a coastline about 1450 km long (Flinn, 1974).

The research has involved field study on all the major islands of Shetland, at nearly a hundred separate and disparate localities (see Figure 1.2-2).

Figure 1.2-1b shows the Shetland Isles' position relative to other sections of the Caledonian-Appalachian orogen prior to the opening of the Atlantic. Shetland occupies a key position in the orogen, roughly equidistant from the Scottish, Norwegian and East Greenland Caledonian terrain s. The understanding of the complex geology of Shetland is thus of considerable importance when attempting any stratigraphic or structural correlation across the northern half of the orogenic belt. Also, Shetland geology is likely to be of particular importance when building any palinspastic reconstruction of the orogen as a whole.

1.3. Working definitions.

1.3.1. Rock nomenclature.

Plutonic rocks within the thesis are named according to their modal mineral content, expressed as volume per cent (see Figure 1.3-1, after Streckeisen, 1976 and 1979; Sabine, 1978). Rocks with over 95% mafic and related minerals are referrred to as ultramafic (ultramafites). Where opaque minerals form greater than 5% of the rock the following designation is used:

5-50% opaque minerals : chromite dunite, etc

50-95% opaque minerals : olivine chromitite, etc

95-100% opaque minerals: chromitite, etc

The term ultrabasic (SiO_2<45%) appears in some sections of the thesis, particularly in part 4 , the section reviewing the REE geochemistry of ultramafic and related rock associations.

It should be noted that rigid application of the term ultrabasic when describing many rock associations leads to some practical difficulties. Most ultramafic rocks are also ultrabasic, but ultramafic rocks composed of pyroxene (eustatite 60% SiO_2 and diopside 55.6% SiO_2) are basic (SiO_2 = 45-52%) or even intermediate (SiO_2 = 52-66%). To avoid the rather cumbersome switching of terms from ultrabasic to ultramafic, when describing, what is a lithological continuum, the term ultramafic is used in preference to ultrabasic. It is best, perhaps, that such chemical classification schemes be reserved for the description of magmas and lavas rather than plutonic igneous rocks. Here, basic and ultrabasic magmas may crystallize to yield mafic and ultramafic plutonic rocks.

1.3.2. Cumulate terminology

The principles of cumulus theory were first detailed by Wager and Deer (1939) and developed in later publications (Wager, Brown and Wadsworth, 1960; Jackson, 1967), culminating in the primary reference work of Wager and Brown (1968). The term cumulate was coined to describe igneous rocks formed by crystal accumulation in layered intrusions. Wager and Brown (1968) described in detail the processes of cumulate formation. First, nucleation and crystallization occurs at the cooling margins of the magma chamber, the crystals, being denser than the magma, tending to sink towards the chamber base. This crystal sedimentation results in a cumulate pile that shows good lamination, but no sorting of contrasting minerals or grain sizes. Large scale convection, induced by temperature differences between the roof and base of the cooling magma chamber, redistributes the cumulus crystals. Changes in convective regime or gravity induced slumps of masses of unconsolidated crystals from the chamber walls result in size and mineral graded rhythmic layers. The accumulated crystals on the magma chamber floor are subsequently cemented by crystallization of the trapped pore liquid (intercumulus liquid). The minerals which solidify from the intercumulus liquid are called postcumulus minerals. If equilibrium is maintained between the crystallizing intercumulus liquid and the main magma reservoir postcumulus minerals would be essentially unzoned, the resultant rock is termed an adcumulate. In the case where the crystallizing intercumulus liquid acts as awclosed system, chemically zoned postcumulus phases result and produce an orthocumulate rock. Progressive fractionation of the main magma body results in cryptic variation; input and mixing of primitive magma from below gives rise to cyclic cumulate layering.

The formation of layered igneous rocks by mechanisms of crystal settling, as outlined above, has been seriously questioned in more recent works (eg. Campbell, 1978; McBirney and Noyes, 1979). It was first noted by Bottinga and Weill (1970) that cumulus plagioclase was less dense than its proposed parental liquid and would be likely to float, a conclusion later confirmed by experimental study (Murase and McBirney, 1973). Plagioclase cannot therefore be a cumulus phase under the Wager and Brown-type crystal-settling model; an alternative mechanism has to be invoked to account for observed plagioclase rich layers within layered igneous rocks. A further problem for the cumulus process is posed by the fact that silicate liquids can behave in a non-Newtonian manner, ie. they can sustain a shear stress, which inhibits crystal movement. High stresses (600-20000 dynes cm^{-2}) must be exerted by crystals before they overcome the yield strength of many silicate melts. Experimental studies have shown that the yield strength of the liquid increases markedly as the melt anneals and polymerizes at lower temperatures (Murase and McBirney, 1973). For olivine and pyroxene crystals to settle in a typical basaltic liquid they must achieve a grain size of about 3 cm to overcome a yield strength of about 600 dynes cm^{-2} (cf McBirney and Noyes, 1979, Figure 3).

Campbell (1978) levels another major criticism at the cumulus process. The theory states that crystal nuclei form at randon centres in the melt (homogenous nucleation), and these crystals are then affected by gravitational forces. However, widespread homogenous nucleation in large slowly cooling magma chambers, such as layered intrusions, would require high degrees of supercooling. This lead Campbell (1978) to conclude that heterogenous or self-nucleation, where nuclei develop against the margins of pre-existing crystals in the intrusion or at the magma chamber margins, is the most likely mechanism for cumulate crystal production.

It has also been noted that layering within fractionated basic complexes commonly lies parallel to the margins of the intrusion, and often at a high angle to the presumed palaeohorizontal, (eg. Casey and Karson, 1982). It is hard, if not impossible, to envisage a situation where such layering could be produced by crystal settling.

These fundamental flaws, in the traditional cumulate hypothesis, lead McBirney and Noyes (1979) to propose an alternative and attractive hypothesis for the production layered igneous rocks. The alternative hypothesis states that cumulate formation takes place essentially in situ, in a static boundary layer of magma at an advancing front of solidification. The static boundary layer of magma, at most a few metres wide, separates the already solidified rock from convecting magma still above the liquidus temperature. A zone of shear is produced by differential movement between convecting and static magma, and a temperature gradient is set up between crystalline marginal material and the liquid. Crystallization proceeds in response to an outward diffusion (towards the margin) of the silicate components and an inward diffusion (towards the centre of the intrusion) of heat. Further refinements of the hypothesis, eg. Irvine (1980), Tait et al., (1984) and Sparks et al., (1984), have given a "double-diffusive convection" model which provides an elegant explanation for many of the observed features of layered igneous complexes eg grading, rhythmic layering, igneous lamination, plagioclase phase layering and high-angle layering, etc. However, McBirney and Noyes (1979) do not seriously challenge the textural observations of the earlier workers, and their cumulative glossary remains essentially intact. Although these terms were developed under the assumption that the rocks were formed by crystal settling they are still widely used by workers in igneous petrology.

Irvine (1982) has partially modified and redefined many of the cumulate terms. He defines a cumulate as "an igneous rock characterized by a cumulus framework of touching mineral crystals or grains that were evidently formed and concentrated primarily through fractional crystallization". Irvine's terminology is used throughout the thesis (see Table 1.3-1). His glossary, although based on the work of Wager et al., (1960), Jackson, (1967), Wager and Brown, (1968), avoids reference to gravity settling as an essential cumulate mechanism. Irvine also recognises the probable existence of accretion cumulates, that are formed essentially in situ; depositional cumulates, that form by deposition from magmatic currents; flotation cumulates, that originate from crystal flotation, and precipitation cumulates, that originate by crystal settling.

1.3.3. Serpentinite terminology.

Many ultramafic rocks, particularly olivine-rich peridotites are, to varying degrees, altered to a hydrous secondary mineral assemblage (serpentinized). Where alteration is advanced the study of the secondary serpentinite textures can give valuable information on the mineralogy and petrography of the ultramafic protolith, and on the physical and chemical conditions of serpentinization.

Serpentinite petrology and petrogenesis has been reviewed extensively by Selfridge, (1936), Deer et al., (1962), Coleman, (1971), Moody, (1976), Wicks and Whittaker, (1977), Wicks, Whittaker and Zussman, (1977), and Maltman, (1978). The effects of hydrous alteration, as observed in thin section, can in general be divided into three categories: pseudomorphic textures formed after olivine, pyroxene, amphibole, talc and chlorite; non-pseudomorphic textures, either overprinting the primary minerals or earlier pseudomorphic textures; and textures of serpentine veins. A comprehensive glossary of terms describing serpentine textures is given in Wicks and Whittaker, (1977) and Maltman, (1978). Their terminology is used througout the thesis when describing serpentine textures and identifying the component minerals.

1.3.4. Primary, primitive and parental magmas.

Primary magma was defined by Turner and Verhoogen (1960). Primary magma is the liquid which separates from, or becomes partially or completely chemically isolated from residual peridotite mantle after some partial melting event, which is temporally directly related to an eruptive event. Thus a primary magma is unmodified by differentiation processes (such as fractional crystallization, volatile loss, contamination, liquid immiscibility, and magma mixing) following segregation from the mantle residuum and entry into some higher level magma chamber or is erupted.

Primary magma, so defined, includes liquids generated by equilibrium partial melting, perfect fractional melting, perfect fractional melting with aggregation of the melts close to the source region and dynamic or continuous melting (also fairly described as imperfect fractional melting).

One of the purposes motivating the search for primary magma is the possibility of applying phase equilibria studies to the liquid in order to predict, with increasing assumptions:

(a) the depth of magma segregation,

(b) the mineral assemblage of the residuum,

(c) the composition of the source mantle from which the magma and residuum were derived.

Objective (a) and (b) can be realised in all cases except for that of fractional melting with melt aggregation separate from the residuum before transport to the surface. Objective (c) can only be realised for cases of equilibrium partial melting. Aggregation of melts produced by fractional melting may appear improbable as a model for static source regions, but it is a reasonably likely situation at the mid-ocean ridges (Pallister, 1984). Ascending mantle becomes progressively more melted as it ascends. If melts separate rapidly into fissures then the liquid in those fissures represents a mixture of fractional partial melts developed at successively higher temperature intervals above the solidus of the source peridotite, but at successively lower pressures, ie the primary magma of the mid-ocean ridges may be a steady-state aggregated product of polybaric fractional partial melting.

During studies of igneous provinces it is sometimes possible to identify the existence of a more magnesian liquid than any commonly erupted or available for study, eg. on the basis of the most magnesian olivines precipitated in cumulates, the bulk composition of cumulates, plutonics and eruptives (as in ophiolite sections), by trace element modelling of cumulates or by experimental study. Within a series of basalts thought to be derived from a common mantle source, but modified from the primary composition to different extents by differentiation processes, those liquids which most closely resemble the primary magma are termed the most primitive. While it is tempting to refer to such liquids as primary it is more cautious to refer to them as primitive, envisaging the possibility of modification of the magma composition between the primary state and its arrival in the crust or volcanic superstructure. Primitive magmas have the highest wt% MgO content, the highest values of Mg/(Mg + Fe), the lowest incompatible trace element concentration and highest compatible trace element concentration of the particular magma series.

In a particular volcanic province it is usually possible to identify a relatively basic lava composition whose abundance and chemistry make it a suitable choice, as the parental magma from which other less basic lavas might have been derived "down the liquid line-of-descent".

Identification of a parental magma in certain differentating magma chambers is intrinsically difficult. Often in deriving a parental magma workers assume a single stage evolutionary process is proceding in some magma chamber which is periodically tapped to provide basaltic lavas. If the magma chamber is also periodically recharged with primitive or primary magma, or if fractional crystallization is proceeding at more than one pressure or volatile content (a more realistic geological situation) then modelling the parental magma becomes problematical.

For example, in a periodically recharged, periodically tapped, fractionating magma chamber a steady-state lava composition may be reached whose chemistry (relative to that of the primary, primative or true parental magma being fed into the chamber) is determined largely by the ratio of the mass fractions deposited as crystal cumulates to the mass fraction escaping as lava. Any change of the ratio of the mass fractions leads to a new steady state. A rise in the proportion ending up as cumulate will lead to a second steady state of higher Fe/Mg ratio and higher incompatible element concentrations. The first steady state magma is not parental to the second, indeed in many cases it will be easy to show that no plausible closed or open system fractionation can lead directly from the first steady state liquid as parental magma to the second. Yet, the relative abundance and many aspects of the chemistry would encourage the misidentification of the first steady state liquid as the parental magma of the province.

1.4 Previous research

1.4.1 Early accounts (1774-1900)

The early history of Shetland ultramafites is rather fragmented with the first reference to talc and 'ironstone' (serpentinite) in Unst by Glow, who visited the islands in 1774, but not published until 1879. Jameson (1798, 1800, 1813) produced an early outline description of metamorphic minerals from Shetland. Hibbert (1819-1822), in the most important of the earlier works on Shetland, mentions the presence of brucite and chromite and published the first geological maps of the islands. Heddle (1878, 1879) provided detailed accounts of minerals and mineral localities, many associated with altered ultramafic bodies, within the metamorphic rocks of Shetland. Heddle's accounts also discuss the age and possible correlation of Shetland metamorphic rocks.

1.4.2 More recent work (1927-1972)

Several decades were to elapse before systematic study of Shetland ultramafites. Phillips (1927, 1928) provided the first mineralogical and petrological description of serpentinized ultramafites from Unst and Fetlar (now the Shetland ophiolite) and various localities from the northern Shetland mainland. It is clear from Phillip's petrological descriptions that he recognised many of the lithologies which make up the Shetland ophiolite.

A 1:10,000 survey of the geology of Shetland was undertaken in the early 1930's by the Geological Survey, with the mapping of the entire group of islands (Summ. Prog. 1930-1935). Read (1934, 1936, 1937), largely as a result of work done on the survey, published a series of classic papers on the geology of Unst. One paper, by Read on the polymetamorphism of the Valla Field block on Unst, is rightly regarded as the starting point of the modern study of polymetamorphic geology. Read's work covering the metamorphic geology of Unst also includes detailed petrographical descriptions of the main lithologies of what is now termed the Shetland ophiolite. Read also detailed the distribution and petrography of the zoned ultramafic bodies in the Valla Field block, Unst. The development of talc-magnesite-chlorite rocks from various serpentinized ultramafite masses in Shetland, along with further details of the petrology of ultramafites from Unst were described by Amin (1952, 1954).

Investigations, by various workers, covering rocks of economic interest give a number of references to ultramafites and associated rocks in Shetland. Strahan et al. (1916) includes a listing of the chromite, talc and steatite resources in Shetland. The history of early chromite exploitation on Unst has been documented by Hitchin (1929) and Sandison (1946), with an account of more recent explorations given by Rivington (1953). Additional references to the serpentine, talc, magnesite, and chromite resources of Shetland were given by Macgregor et al. (1940), Wilson and Phemister (1946) and the Scottish Council - Development and Industry (1954).

The next phase of investigation of Shetland geology was developed by Derek Flinn in a series of important papers covering the stratigraphy, structure and metamorphic history of large areas of the islands. Flinn (1952, 1956, 1958) detailed the deformation, and structural and lithological units of the Shetland ophiolite, particularly the melange units, on both Unst and Fetlar. Miller and Flinn (1966) provided the first survey of age relations of the main tectonometamorphic and igneous events. This paper defined many of the tectonostratigraphic units used in later publications. An account of the structural and metamorphic history of, what Miller and Flinn defined as, the East Mainland succession from the southern part of the mainland is given by Flinn (1967). Lithological, metamorphic and structural descriptions of the Dunrossness spilite group and Quarff tectonic melange rocks, along with detailed maps of the south mainland, are given in this paper. Later, Flinn et al. (1972) reinterpreted the tectonostratigraphy of the east Mainland and correlated the East Mainland succession with the Moine and Dalradian of the Scottish Caledonides.

Phemister (1964), in a follow-up paper to work done originally on the survey, described rodingites forming irregular vein- or dyke-like bodies in the antigorite-serpentinite at the base of the upper allochthon on Fetlar (now the Shetland ophiolite). Phemister suggested that the rodingite bodies were derived from gabbroic dykes or rafts in the ultramafite, modified by metasomatic interaction of the two lithologies.

Regional gravity and magnetic total field coverage of Shetland was obtained by McQuillin and Brooks (1967) and during the aeromagnetic survey of the U.K. (Geological Survey, 1968). In the aeromagnetic survey the area was surveyed along E-W flight lines 2 km apart, with a mean terrain clearance of about 300 m and with tie lines at 10 km intervals.

Early geochemical studies of Shetland rocks included analyses of ultramafites and steatites. Gill (1965), in a doctorate thesis on the petrology of the Brae plutonic complex, provides useful whole-rock and mineral geochemical data for ultramafites, gabbros, diorites and granodiorites. Flinn (1970) presented a collation of previous and new whole-rock major element data for the metamorphic rocks of Unst and Fetlar. This data includes analyses of serpentinized peridotites and a pyroxenite, along with gabbros, diorite, quartz-albite porphyry and albite granophyre (plagiogranites) from the main nappe sequence and melange units of the 'Layered complex' (Shetland ophiolite). Flinn concluded that the ultramafites belonged to a typical Alpine-type complex (sensu Thayer, 1967). In a study of the zoned ultramafic bodies on Unst, Curtis and Brown (1969, 1971) detail the major and trace elemental distribution within the mono-mineralogical zones. A detailed assay and map of steatite resources from Cunningsburgh, Dunrossness spilite group is presented by Bain et al. (1971).

1.4.3 Recent work (1973 - present)

Current interest in ultramafites from the Shetland Caledonides stemmed from the identification by Flinn (pers. comm. in Garson and Plant, 1973) that the 'Layered complex' on Unst and Etlar represents an obducted ophiolite. The first contemporary account of the Shetland ophiolite is presented by Flinn et al. (1979). Other recent studies on the Shetland ophiolite have centred around the economic potential of chromite and associated platinum group metal deposits within the complex by the Geological Survey and Open University (Plant et al., 1975;

Cogger, 1980; Pritchard and Neary, 1981; Gass et al., 1982). Other references to the Shetland ophiolite include: Thomas (1980), which contains a table of major and limited trace element data on the 'serpentinites' and 'gabbros' (unfortunately the locations of the analysed rocks is not given); Bartholomew (1984) on structural features of the upper mantle section of the ophiolite on Unst; Taylor (1984), a geophysical investigation, in which Taylor, with data little improved on that of the Geological Survey, attempts to model the three-dimensional structure of the ophiolite on Unst; Pritchard (1985), a short general description of the complex.

Two recent papers by Barber and Soper (1982) and Dewey and Shackleton (1984) regard the Shetland ophiolite as structurally important within the context of Scottish Caledonian geology. Both sets of authors look to the Shetland ophiolite as a remnant of a single supra-Grampian ophiolite sheet responsible for burial and consequent metamorphism of the Grampian tract. However, petrological (Read, 1934; Flinn, 1958; Aziz, 1984) and radiometric age data (Spray, 1984) indicate that the formation and obduction of the Shetland ophiolite significantly post-dates the Grampian D3 metamorphic peak (cf. Watson, 1984).

Garson and Plant (1973) also identify the Dunrossness spilite group as an ophiolite complex, but produce no supporting evidence. They correlate the Dunrossness spilite group with the Portsoy sill, of the Grampian Highlands and Tayvallich volcanics. The assertion that the Dunrossness spilite group represents an ophiolite was taken up by Henderson and Robertson (1982), who suggested a three-way correlation with the Highland Border Complex and Shetland ophiolite.

Other publications of direct relevance to the geological setting of Shetland ultramafites are referred to in the main body of the thesis. Perhaps the most significant are: Pringle (1970) and Robinson (1983), both on the metamorphic rocks W of the Walls Boundary fault; Mykura and Phemister (1976) on the geology of western Shetland and in particularly the Walls metamorphic series; Flinn (1985), an up to date summary review of Shetland pre-Caledonian, Caledonian, and Devonian and younger rocks.

1.5. Methods of study.

1.5.1. Field techniques.

All the known ultramafic bodies on Shetland were mapped on a 1:10,000 scale with the exception of the Shetland ophiolite where select transverses were taken through the principal ultramafic units. Many of the smaller and/or more complex ultramafics were mapped in finer detail on home-made base maps or photographically enlarged versions of the 1:10,000 scale O.S. sheets. As previously stated, mapping involved field observation and mapping at over a hundred separate localities throughout the islands.

A flux-gate magnetometer was used extensively during field mapping. During serpentinization of the ultramafic rock magnetite is invariably produced, particularly from the secondary alteration of olivine. As a consequence of the alteration the ultramafic units usually possess an easily definable magnetic anomaly with respect to the surrounding weakly magnetic country rock. The shape and polarity of the magnetic anomaly was used to define the margins of the ultramafic bodies, its depth from the surface and occasionally its three dimensional form. The edge of an individual body, in areas of poor exposure, was taken to be where a significant variation in the magnetic intensity was observed. The depth to the magnetic body being derived using the equations in Dobrin (1976). The 3-D shape of a magnetic body can be deduced from the distribution and polarity of the magnetic anomaly. Accepting that the magnetic body behaves as a simple di-pole one is able to define, from the relative magnetic effect, the geometric form of the body. For example, a vertical sheet-like body (essential infinite in the third dimension) will have no associate negative anomaly adjacent to the positive anomaly of the causative body. Similarly, other geometric forms can be recognised from their magnetic effect (cf. Dobrin, 1976).

The flux gate magnetometer used was easily portable and allowed rapid surveys to be made, the primary aim being to define the margins of the ultramafic unit rather than make an accurate geophysical study. The model used measured variations in the vertical magnetic field to a precision of about 5 gammas.

1.5.2. X-ray fluorescence spectrometry (XRF).

1.5.2.1. Introduction

Eighty-three samples from various major and minor ultramafic units on Shetland were analysed. Whole rock major and trace element determinations were done by standard XRF analytical techniques. Sample localities and their geological setting are discussed later in the relevant sections.

1.5.2.2. Principles of the technique.

A specimen may be made to emit X-rays by irradiating it with polychromatic X-rays (white radiation) so that fluorescent X-radiation is emitted. This characteristic secondary radiation emitted from within the analysed sample is produced as a response to primary radiation falling on to the sample and causing ejection of inner orbital electrons. The atoms regain stability by successive electron transitions from states of higher to lower energy with secondary radiation emitted for each electron transition. The wavelength of the characteristic radiation emitted is inversely proportional to the difference of the initial and final energy states of the transferred electron.

The secondary radiation produced is analysed by counter spectrometers. Figure 1.5-1a illustrates a conventional arrangement for fluorescence work. Various types of fluorescence spectrometer are available using flat reflecting, curved transmitting or curved reflecting crystal analysers. The curved reflecting type analyser is illustrated in Figure 1.5-1b. Two X-ray detector (counter) systems are normally employed to analyse the secondary radiation. A gas flow proportional counter is generally used for longer (softer) wave lengths (>3Å up to 12Å) X-rays photons entering the counter ionise the gas, usually a mixture of argon and methane, producing electrons and positive ions. The electrons move towards a central anode wire and the positive ions move to the earthed casing of the detector. As the ions and electrons separate there is a sharp drop in the voltage which takes several hundred microseconds to return to the original value; this being due to the relatively high velocity of the electrons compared to the positive ions. The pulses of voltage produced can be counted and used to deduce the intensity of fluorescent X-radiation for any particular wavelength. The scintillation counter is used for shorter (harder) wavelengths (0.38Å - 2Å) and consists of a phosphor and an photomultiplier. The phosphor converts the X-ray photons into (blue) light and the photomultiplier converts the light pulses into voltage pulses which in turn can be counted. This counter has a very short dead time (0.2 μ sec) ensuring linear counting up to very high intensities.

The intensity of the emission lines produced are dependent on the amount of the corresponding elements present in the sample. Given a suitable calibration the wavelength and intensity of X-ray emittion is used as a tool for quantative analysis of the rock chemistry.

1.5.2.3. Analytical procedure.

Sample preparation. Whole rock samples were obtained by diamond sawing 100-150 g blocks from hand specimens selected on the basis of previous petrographic work. Blocks from each sample were crushed in a mechanical jaw crusher down to an aggregate of rock chips ca. 0.2-0.5 cm^3. Approximately 100 g of rock powder (<100 mesh) of each sample was then prepared by further crushing in a clean tungsten-carbide Tema. Care was taken to ensure that the samples were homogenous prior to milling. The samples were then hand crushed using an agate pestle and mortar and sieved to less than 53 µm.

The fine rock powders (<53 µm) were then used to prepare fusion disks for whole rock major element chemistry determination and powder pellets for trace element analysis. For the powder pellets, 5-7 g of rock powder was mixed with an organic binder (Moviol) and pressed using an hydraulic ram into a 3.5 cm diameter disk. In the preparation of the fusion disks c 0.6200 g of fine rock powder was accurately weighed and mixed with a $Li_2O.2B_2O_3/Li_2CO_3/La_2O_3$ flux mixture (trade name Spectroflux 105), at a rock to flux ratio of 1:5.4321. The rock plus flux samples were then fused by heating to 1000 °C in platinum crucibles and pressed into disks on aluminium plattens. The fragile fusion disks were mounted on bakelite backing disks to protect the sample during handling and XRF analysis.

Elemental analysis. All samples were analysed at the University of Liverpool Geology Department on a Siemens SRS1 XRF machine. Analysis was aided by partially automated sample changing and data aquisition directed by a dedicated Apple II computer system.

Trace elements analysis of powder pellets was done using the method of Brown et al., (1973) with raw data from the machine analysed using a slightly modified version of their Fortran program (MAJOR) on the University's 1906 ICL computer. Synthetic primary standards were employed: pure SiO_2 (BLK), pure SiO_2 "spiked" with a known concentration of trace elements (MESS1) and (MESS2) and a pellet of andesitic composition (SPA) containing major elements, but no trace elements other than Ti. These monitored experimental drift. Major element analysis on fusion disk samples followed a similar procedure with departmental standard GL 10 used as a monitor. GL 10 is a granite from Donegal. Additional standardization, for both major and trace elements, was also performed against USGC standard rock BCR-1.

Table 1.5-1 lists the operating conditions for X-ray fluorescence spectrometry on powder pellets for major elements and fusion disks for trace and rare-earth element analysis.

1.5.2.4. Results

Results from six replicate analyses of a Dunite BU423 which was used as a personal standard are listed in Table 1.5-2. Sample BU423 was run in six separated batches along with departmental standards to monitor run-to-run precision. Coefficients of variation ($100\sigma/x$) were determined for each element based on all six runs of BU423. Run-to-run precision is assumed to be roughly equal to the variation seen in the six analyses of BU423 (Table 1.5-2) and can be considered to represent a measure of machine error. Percentage variations between replicate analyses are very low for all elements at abundance levels higher than the lower limit of detection. For elemental concentrations, at or below, the stated lower limit of detection (Table 1.5-1) precision is relatively poor and therefore such values have to be used with caution.

Results from two replicate analyses of four different ultramafic rocks from various parts of Shetland are listed in Table 1.5-3. Each of the four rocks was split after initial jaw crushing with each half treated separately throughout the rest of the sample preparation and analysis procedure. Variation between analyses therefore represents not only run-to-run error but also sample-to-sample error limits. The results show that for virtually all elements variation acquired during sample preparation and analysis is less than, and indistinguishable from, the machine error ie the values are within run-to-run precision (% coefficient of variation). The few values which do differ by greater than the percentage run-to-run variation (asterisked in Table 1.5-3) are probably the result of incomplete homogenisation of the sample prior to its division during the various stages of the crushing procedure. No one element gives systematically erroneous results which might indicate varying degrees of external contamination.

Full whole-rock major and trace element data are presented in their relevant sections throughout the thesis.

1.5.3. Radiochemical neutron activation analysis (RNAA).

1.5.3.1. Introduction.

Rare earth element determination were made by radiochemical-separation instrumental neutron activation analysis (RNAA) at the Universities Research Reactor, Risley, near Warrington. The method used is detailed in Duffield and Gilmore, (1979). Radiochemical separation of the REE group was used in preference to the widely used INAA schemes. REE determination by purely instrumental methods (INAA) is hampered by matrix activation (interference from other elements in the sample), post-irradiation separation avoided potential errors due to interference. It also minimised counting times and ensured all 14 REE could be measured. The elements La, Ce, Sm, Eu, Yb, Lu are measurable by almost any reasonable radio activation scheme, including purely instrumental schemes. Pr, Gd, Ho and Er, however, have poor cross-sections, low isotopic abundances and activate to produce isotopes with inconvenient half-lives. These 'difficult elements' are immeasurable in whole rock and present problems even in the chemically separated REE analytical techniques due to the high activities of ^{140}La, ^{153}Sm and ^{152m}Eu, particularly in rocks with low heavy REE concentrations. Measurement of Nd, Tb and Tm is only satisfactorily accomplished after decay of the major activities. Dy presents different problems due to the short half-lives of the activation products.

The scheme described here pays special attention to the measurement of the 'difficult elements'. The procedure involves irradiation, REE group separation and three γ-spectrum measurements in order to determine all REE with the exception of Dy. The chemical yield and Dy concentration are measured after re-irradiation of the REE separates.

1.5.3.2. Sample preparation.

Samples were analysed in batches consisting of eight samples and two aqueous standard solutions. Approximately 500 mg of each powdered rock sample was weighed into 1 ml aluminium vials and sealed. Approximately 400 mg of each standard solution was accurately weighed into glass tubes and sealed. The standard solutions consisted of Johnson Mattey "Specpure" rare earth oxides (with the exception of Ce) in dilute nitric acid. Cerium oxide was dissolved in concentrated sulphuric acid, taken to dryness and then dissolved in nitric acid. Aqueous standard CRE1 contained La, Nd, Eu, Dy, Tm, Yb, Lu, and CRE2. The elemental concentrations were chosen to be representative of a 'typical rock' with the concentration of the 'difficult elements' enhanced.

1.5.3.3, Irradiation.

The eight samples and two standards were placed together in an aluminium irradiation container and irradiated for about 9 hours in the Universities Research Reactor 1, ½" central vertical hole, reactor power 300 KW, with an estimated flux of approximately 3 x 10^{12} n. $cm^{-2}.s^{-1}$.

1.5.3.4. REE group separation.

Following irradiation the rock samples were extremely radioactive and all manipulations were carried out behind lead bricks and in a fume cupboard to minimise radiation exposure to the analyst. The aluminium sample tubes were prised open and the sample tipped into a 15 ml platinum evaporating basin containing 1 ml La^{3+} carrier (10 mg/g). The empty vials were weighed to derive the actual weight of the samples used. Sample and carrier were mixed and 10 ml 40% HF added. The sample was then evaporated to dryness on a sand bath heated to 150 °C. The evaporation was repeated with a further 10 ml of 40% HF and then with a mixture of 5 ml 40% HF and 5 ml conc $HClO_4$.

The dried contents were washed in a 125 ml beaker with conc HCl and 10 ml saturated borax solution added to complex any fluoride remaining and the residue then dissolved by boiling. A mixed hydroxide precipitate was then formed by neutralizing the mixture with NH_4OH. The hydroxide precipitate was then dissolved in HCl and NH_4F at pH5. The resultant fluoride precipitate was centrifuged, washed and redissolved in HCl and saturated boric acid.

Slight traces of silica, occasionally present at this stage, were removed by filtration. The REE solution was then diluted to 30 ml and NH_4OH added, again producing a hydroxide precipitate. The solution was cleaned with a few drops of dilute HCl, heated to boiling and 30 ml saturated oxalic acid added; the mixed rare earth oxides precipitating on cooling. The final gel-like oxalate precipitate was drained of excess liquid, washed twice with H_2O and once in acetone and transferred to a 3 ml polyethylene counting vial. The REE oxalate concentrate is then evaporated to dryness in an oven. Standard solutions were transferred into centrifuge tubes containing 1 ml La^{3+} carrier solution and the oxalate precipitation procedure performed on them and the precipitate dried.

1.5.3.5. Counting procedure (gamma-spectrometry).

The first of four counts were made using a sample changer, operated overnight, the sample-to-detector cap distance being either 4 or 10 cm depending on the activity of the sample. Each sample was counted for 3000 s live time. The second count was usually made the following day, with a 300 s live time. A third count was made after 10-12 days decay for a count period of 3000 s live time. Table 1.5-4 lists the counts in which γ-rays were measured for the different REE isotopes. The counts used were determined by two main factors; the half life of the isotope, and the amount of peak interference at the time of counting. Clearly short lived isotopes need to be measured soon after irradiation. Whereas the longer lived isotopes Nd, Yb, Ce, Lu (Table 1.5-4) are more reliably measured during the third count when γ-ray interferences from the other REE is minimal.

Dy was measured using the ^{165m}Dy isotope which has a half life of 1.3 minutes. After the third count, the oxalate precipitates were individually reirradiated for 30 seconds in the URR rabbit tube (flux ≈ 3 x 10^{12} n. $cm^{-2}.s^{-1}$). Samples and standards were counted for a fourth period (200 s live-time) after a 90 s decay time. ^{140}La was measured along with Dy in order to estimate the chemical yield of the separation.

Gamma-spectra were measured using a Ge(Li) detector of 2.4 keV FWHM (at 1332 keV) and 10% efficiency relative to NaI(Tl) with a 4 K multi-channel analyser system based on a CAMAC interface and NOVA 1200 computer. The system recorded time-of-year at the start of counts, real and live times of acquisition.

1.5.3.6. Results.

Elemental concentrations were calculated using a BASIC program, CTRE. Peaks were detected by the gaussian correlation method of Black (1969) and peak areas calculated by the total peak area method using a peak width dependent on energy. CTRE makes the following corrections to the measured peak areas: live time; coincidence loss calculated from the expected and observed count rates of the electronic pulser peak; chemical yield correction derived from the ^{140}La peak areas in the final γ-ray spectra measured after re-irradiation; decay from the end of irradiation and during counting, and the growth of activity during irradiation.

Least square peak analysis was necessary for some γ-ray spectra (Table 1,5-4). Where peak areas were small eg 363 keV γ-ray of ^{159}Gd and 308.2 keV of ^{171}Er, the least square analysis method gives considerably better precision of actual peak area. Similarly, the method was used to separate overlapping peaks such as the 84.3 keV γ-ray of ^{170}Tm and the 86.6 keV γ-ray of ^{160}Tb.

Element concentrations are derived by comparison of corrected peak areas of samples and standards. Results are quoted as the weighted mean of the concentration deduced from the various counts using the total counting variance as a weighting factor. Relative standard deviations of the peak areas were also calculated and are listed alongside the actual result.

1.5.4. $^{40}Ar/^{39}Ar$ step heating method.

1.5.4.1. Introduction.

Most of the dating of Shetland rocks has been done by the conventional K-Ar method (Miller and Flinn, 1966). This method depends on two basic assumptions: first, that the sample contains no argon at the time of its formation, the ^{40}Ar which occurs being produced by decay of naturally occurring ^{40}K by electron capture and positron emission, and second, that all radiogenic argon produced within the sample is retained. It has been demonstrated that argon may be lost by diffusion even at low temperatures well below the melting point. A K-Ar date therefore records the time elapsed since cooling to a temperature (blocking temperature) below which loss of argon by diffusion is insignificant. In slowly cooling systems eg rocks within an orogenic pile, the K-Ar closure is by definition likely to be significantly later than any principal tectonothermal or intrusive igneous episode. Invariably K-Ar dates have to be interpreted with caution. The K-Ar system can be assumed to be open to Ar diffusion until the rock is cool. Where a blocking temperature for the dated material can be defined, eg. biotite c. 300 °C and muscovite c 350 °C, K-Ar dates can be useful in delimiting the age and rate of exhumation of a metamorphic terrain (Harper, 1967).

Problems also arise in K-Ar dating where, under certain circumstances, excess radiogenic argon may be present which causes K-Ar dates to be too old. With the conventional K-Ar method there is no way of identifying such dates. Other possible complications in K-Ar date interpretation also arise, for example, if a rock or mineral formed at time A is reheated and undergoes partial outgassing at a time B the resultant K-Ar date will be an apparent age somewhere between time A and B.

Studies by Dalrymple and Lanphere (1971) and Mussett et al. (1980) have shown that the $^{40}Ar/^{39}Ar$ method can give significantly better dating accuracy than the K-Ar method, especially when using samples with a complex thermal history. The $^{40}Ar/^{39}Ar$ step-heating method gives an age spectrum which partially reflects the samples thermal history. Using an age spectrum (see Interpretation of age spectra, Section 1.5.4.4.) it is possible to identify partial resetting events and to reject from the age calculation certain low temperature steps formed by loosely held contaminating argon. An additional advantage of the $^{40}Ar/^{39}Ar$ dating technique is that only measurements of the isotopic ratios are required. In the K-Ar dating method measurements of the absolute abundances of ^{40}K and ^{40}Ar are required and thus in some cases inhomogeneities in the sample can lead to inaccuracy.

The only real disadvantage with the $^{40}Ar/^{39}Ar$ step-heating method is that it is time consuming, taking about five laboratory days to produce one date.

The low K content of the various serpentinised ultramafic rocks on Shetland preclude their direct use in $^{40}Ar/^{39}Ar$ dating. Dating has been carried out in K-bearing mafic minerals or mafic lithologies intimately associated with two important ultramafic units: the Brae plutonic complex (Section 3.1) and the Dunrossness Spilite group (Section 2.6).

1.5.4.2. Principles of the method.

The $^{40}Ar/^{39}Ar$ method of dating is based on the convertion of ^{39}K, the common isotope of potassium, to ^{39}Ar by fast neutron irradiation, under the reaction

$$^{39}_{19}K\ (n,p)\,^{39}_{18}Ar\quad .$$

Here the ^{39}Ar produced is treated as stable, though it does decay very slowly back into ^{39}K by beta emission (half life of 269 years), ie. it is essentially stable during the short period of time involved in the analysis. The number of ^{39}Ar atoms produced on irradiation is calculated using the formula of Mitchel (1968),

$$^{39}Ar = {}^{39}K\Delta T \quad \psi(\epsilon)\sigma(\epsilon)d\epsilon,$$

where ^{39}K is the number of atoms in the irradiated sample, ΔT is the length of irradiation, $\psi(\epsilon)$ is the neutron flux density energy ϵ, $\sigma(\epsilon)$ is the capture cross section of the ^{39}K for neutrons having energy ϵ, and the integration is carried out over the entire energy spectrum for the neutrons. Given that the proportion of ^{39}K converted to ^{39}Ar is known, and the number of radiogenic ^{40}Ar atoms present in the sample due to decay of ^{40}K is

$$^{40}Ar^* = \frac{\lambda e}{\lambda}\,{}^{40}K(e^{\lambda t} - 1)\ ,$$

where λe is the decay constant of ^{40}K for election capture and λ is the total decay constant for ^{40}K. A measurement of the $^{40}Ar^*/^{39}Ar$ ratio can be obtained, where

$$\frac{^{40}Ar^*}{^{39}Ar} = \frac{\lambda e}{\lambda}\ \frac{^{40}K}{^{39}K}\ \frac{1}{\Delta T}\quad \frac{e^{\lambda t} - 1}{\psi(\epsilon)\sigma(\epsilon)d\epsilon}$$

This ratio is equivalent to the $^{40}Ar/^{40}K$, the ratio used in conventional K-Ar dating. However, several parameters in the above equation are difficult to quantitatively evaluate, for example, the neutron flux density and the capture cross section. But by irradiation of a sample of known age (the flux monitors), a parameter J can be calculated from the ratio of $^{40}Ar/^{39}Ar$ in the monitor. Substitutiion of the J value in to the above equation, where

$$J = \frac{\lambda}{\lambda e} \quad \frac{^{39}K}{^{40}K} \Delta T \quad \psi(\epsilon)\sigma(\epsilon)d\epsilon$$

gives us,

$$\frac{^{40}Ar^*}{^{39}Ar} = \frac{e^{\lambda t} - 1}{J}$$

The age of the sample is then calculated using the $^{40}Ar^*/^{39}Ar$ ratio from the following equation,

$$(age)t = \frac{1}{\lambda} \ln \quad \frac{^{40}Ar^*}{^{39}Ar} J + 1$$

The dates obtained in this way are referred to as "total argon release dates" or "total fusion ages" (see Table 1.5-5). This is a simple hybrid of the conventional K-Ar date and subject to many of the same limitations. The $^{40}Ar/^{39}Ar$ method only really becomes a powerful tool for dating when incremental (step) heating is applied to a particular sample. By releasing argon from the sample in steps, at progressively higher temperatures and with dates calculated solely on the $^{40}Ar/^{39}Ar$ ratio for each step, a spectrum of ages is achieved. This spectrum reflects to some degree the thermal history of the specimen.

1.5.4.3. Analytical technique.

The samples dated include two whole-rock metabasalts and two hornblende mineral separates from hornblende gabbros. Cores ca. 1.5 cm diameter were drilled from the unweathered areas of the metabasalts, these cores were cut giving a disk shaped solid sample ca. 1 cm^3 in volume and weighing 2-4 g. The hornblende gabbro samples were lightly crushed in a jaw-crusher to break down the rock into its individual constituent minerals. The samples were then sieved (150μm sieve) to leave a coarse fraction free of contaminatory fine particles from which pristine hornblendes were separated by eye giving a mineral separate weighing 1-2 g. The purity of the separates is estimated at ≈ 99.5% hornblende.

Samples were irradiated at the Herald Reactor, Aldermaston at a flux density of between 3.997 and 4.081 x 10^{17} fast neutrons cm^{-2} over a period of sixteen hours and without shielding of thermal neutrons. The neutron flux density (see J-value above) was calibrated using "standard" biotite samples as flux monitors placed alternately with samples along the length of the irradiation can (J = 0.0025 ± 0.00007 for all samples). The standard used was the Bern biotite 4B for which a mean age and standard deviation of 16.4 ± 0.2 my has been calculated from published data (Steiger, 1964; Armstrong et al., 1966; Armstrong, 1969).

Following this irradiation each sample was heated stepwise by radio-frequency induction up to 1200 °C. Samples were held at particular temperatures for thirty minutes, the gas sample produced at each step then underwent a series of chemical and physical purification processes. Several contaminating gases produced along with argon during heating, mainly H_2O, N_2 and CO_2, were extracted via an array of liquid nitrogen u-tubes and titanium sponges leaving the argon sample pure.

Argon isotopes were analysed using an AEI MS10 mass spectrometer with three repeat counts performed on each gas sample. Peak heights of the argon isotopes were recorded by chart recorder and no systematic change in peak height was observed during a scan. Good peak separation on the chart recorder was attained by a high irradiation dose, converting more ^{40}Ar to ^{39}Ar during irradiation. Peak interference for samples of this age (Table 1.5-5) has in the past given a sizeable measuring error because of the difficulty of measuring true peak heights on a strong sloping background produced by the ^{40}Ar peak.

The measured atmospheric ratio varied from 280.4 to 306.7 during the course of the experiment, but changed slowly and semi-systematically. These monitored variations are allowed for when calculating the effects of atmospheric interference. Similarly, independent checks for the interfering reactions which produce ^{40}Ar and ^{39}Ar from potassium and calcium were carried out by the laboratory. These variables were also included as correction factors in the age calculation. Errors from the interference by isotopes derived from potassium and calcium can therefore be regarded as negligible or non-existant.

1.5.4.4. Interpretation of age spectra.

The incremental heating and release of argon from a sample results in a series of apparent ages or an age spectrum for that sample. It is with the interpretation of such spectra that the ^{40}Ar/^{39}Ar technique becomes most useful.

The release of argon from a sample is a complicated process with several possible mechanisms involved (Mussett, 1969; Harrison, 1983). At its simplest, it is assumed that gas from different sources is retained in sites of different energy and so will be released at different temperatures during stepwise heating. However, in detail the systematics of argon release has proved difficult to model from first principles, the release patterns observed reflecting the fact that a combination of mechanisms is involved. Modelling of the complex release patterns of argon expected under different circumstances has been tested empirically with measurements on artificial samples (Fitch et al.,

1969) and by experimental heating of natural material eg. Harrison and McDougall, (1980) and Harrison, (1981).

Harrison, (1983), in a review of the limitations on the interpretation of Ar/Ar spectra, outlines the principle factors to be considered when assessing any particular argon release pattern. Interpretation is limited by : (a) multiple episodic loss, (b) slow cooling, (c) mixed mineral phases, (d) resolution of the age spectrum, (e) excess ^{40}Ar, (f) recoil artifacts, (g) grain size and (h) phase changes during experimental heating.

(a) Multiple episodic loss. A sample completely closed to argon and potassium since the time of initial cooling will have constant ^{40}Ar*/^{39} ratios hence the apparent age of each heating step will be constant and a single age plateau will be produced. With a partial loss of radiogenic argon at some time after initial cooling the gas released at different steps will have varying ^{40}Ar*/^{39}Ar ratios. Turner (1968) described the age spectra produced with such partial loss of radiogenic argon for aggregates of both uniform and lognormal distribution of spherical radii. More recent studies have used his basic ideas to determine the ages of recrystallized and thermally disturbed samples as well as the amount of ^{40}Ar* lost during the reheating event.

Reheating events can be identified from an age spectrum where only a partial requilibration of the argon isotopes is achieved. Gas released in the initial steps of experimental heating originates from low energy sites, eg. grain surfaces or lattice defects, this gas will have a low ^{40}Ar*/^{39}Ar ratio corresponding to the time of the reheating episode. In higher temperature steps the gas sample has a higher ^{40}Ar*/^{39}Ar ratio, because argon from the more retentative sites has lost less radiogenic argon during the reheating episode(s). With step heating to the highest temperatures argon from the most retentive sites is released. The argon ratios may be uniform at this stage giving a high temperature 'plateau' correlative with the last complete argon equilibration event (plateau age).

Samples which have experienced several reheating/outgassing events can be recognised; the resulting age spectrum containing a series of minor plateaux. However, because of the difficulties of resolving minor changes in $^{40}Ar^{*}/^{39}Ar$ ratios in an age spectrum (see Resolution of the age spectrum, below), only the larger reheating episodes are usually recognisable.

(b) Slow cooling. Recently it has been shown the $^{40}Ar^{*}/^{39}Ar$ age spectra of rocks which have cooled slowly (ca. 5 °C my^{-1}), through the range of temperatures over which $^{40}Ar^{*}$ is retained, have a recognisable and characteristic profile. Such spectra show a linear increase in age over the first 60-70% of the total ^{39}Ar released followed by a plateau (Harrison and McDougall, 1982). The magnitude of the age gradient resulting from slow cooling is strongly dependant on the diffusion geometry of the material analysed. Under a given cooling history, the age spectrum obtained from a sphere has a steeper and broader age gradient than for minerals with a tabular shape (Dodson, 1984). It is not known how slowly cooling would affect the spectra of multiphase samples. They may well be indistinguishable from the spectra of samples which have undergone a partial resetting event or multiple episodic loss.

(c) Mixed phases. The interpretation of thermal events affecting monomineralic samples is relatively straightforward. However, the majority of geological samples are polymineralic and consequently may show complex patterns of argon release. With polymineralic samples where the different phases have different argon release kinetics the age spectra produced are a compound of differing $^{40}Ar^*$ closure times. In these cases the age spectrum produced may be stepped. Resolution of the individual steps (? diffusion profiles) from a single age spectrum may then be tentatively correlated with observed mineralogical and petrographical features in the rock sample.

The partial outgassing of mixed phase samples, where phases with differing argon retentivities are involved, can also result in different apparent ages from phases which originally had the same $^{40}Ar^*/^{39}Ar$ age.

Harrison and McDougall (1981) have demonstrated another complication in dealing with mixed phase material. They have shown that similar effects to those observed from polymineralic samples occur in amphibole samples which contain an exsolved phase.

(d) Resolution of the age spectrum. The argon from a sample is extracted in relatively few finite heating steps and therefore cannot map continuous patterns of argon release produced during heating. Where the $^{40}Ar^*/^{39}Ar$ ratio is rapidly changing ie during the first few percent of ^{39}Ar released from samples that have experienced partial $^{40}Ar^*$ outgassing, the age calculated for each step is invariably a mixture of a plateau age and the age at which $^{40}Ar^*$ loss actually occurred. Similarly, steps containing a large percentage of the total argon released, even where $^{40}Ar^*/^{39}Ar$ rations are relatively static, are likely to be an amalgamation of different Ar/Ar ratios. In working with geological samples resolution is maximised by incremental heating at around 50 °C intervals. Smaller heating steps and consequently lower percentages of argon released tend to result in increased experimental error through air contamination and isotopic fractionation.

(e) Excess ^{40}Ar. It has been seen that often in some terrestial samples the first few percent of argon released yields an ^{40}Ar*/^{39}Ar age significantly older than the plateau age. These older initial step ages are thought to be a result of excess ^{40}Ar and give the age spectrum a characteristic U-shape. The U-shaped spectrum, as illustrated in Fig 5 from Harrison and McDougall (1980), is developed where a sample has undergone partial outgassing during reheating, but before cessation of the thermal event a high concentration of ^{40}Ar developed resulting in ^{40}Ar diffusion into the lower energy sites of the rock.

Samples affected by excess argon do not always develop a U-shaped age spectrum. Pankhurst et al., (1973) found plateau ages which were clearly high but only distinguishable as such by their stratigraphical and geological inconsistency.

(f) Recoil redistribution of ^{39}Ar. The interpretative models outlined above all assume that ^{39}Ar produced during irradiation is distributed in a similar way to the ^{40}K in the sample. However, because of the high recoil energy of the reaction ^{39}K(n,p)^{39}Ar, the possibility that some ^{39}Ar atoms are displaced from their sites by recoil occurs. Under this recoil artifact ^{39}Ar is transferred from near surface regions of crystals into sites with a lower release temperature such as adjacent grains of different composition. Studies have shown (eg. Huneke and Smith, 1976) that the recoil affect on age spectra can be significant in some fine grained samples, where K-bearing phases are adjacent K-poor minerals, causing in some cases more than one apparent age plateau in a single age spectrum.

(g) Grain size and distribution. Ideally during mineral separation an aggregate of grains with similar dimensions to those in the original sample is recovered. Over-crushing of the sample may well affect the result. Here, argon diffusion from grains in which both cores and rims are exposed results in an homogenisation of $^{40}Ar^*/^{39}Ar$ ratios from these different sites and thus yields an incorrect plateau age.

(h) Phase changes. In discussing the various models and artifacts of argon release it has been assumed that gas loss takes place by volume diffusion without significant alteration of the internal Ar isotope distribution. Phase changes by either dehydration or homogenisation of exsolution features during experimental vacuum heating may effect the argon distribution and release patterns of a sample. Hydrous minerals, particularly biotite, are induced to release argon during dehydration. The resulting argon release patterns, because of this complex behaviour, can be chronologically meaningless. Experiments have shown (Zimmerman, 1972), that hornblende is not affected to the same extent as biotite as it does not lose significant quantities of $^{40}Ar^*$ until dehydration is nearly complete.

The homogenisation of exsolved phases in a mineral may also affect argon release as phase boundaries behave as channels for rapid argon diffusion. The exsolution boundaries are destroyed with incremental heating to levels above the homogenisation temperature and are therefore closed to argon diffusion.

1.5.4.5. Results.

The definition of a plateau age is a subjective business. Mussett (1980) adopted the following arbitrary criteria for their recognition, "a plateau must have at least four consecutive steps none of which differ from the mean plateau age by more than their standard deviation, and must comprise at least half of the ^{39}Ar released". Mussett in his work on Tertiary basalts applied these criteria primarily to exclude from the age calculation steps affected by late hydrothermal alteration. In rocks which have undergone several partial outgassing events such strict criteria are inhibitive and often quite major plateaux are rendered unusable. Other workers have been happy to use and interpret plateaux with about 10% of the total ^{39}Ar released, eg. Fitch et al., (1984). Dalrymple and Lanphere, (1974) adopt a plateau size limit of 4-5% of the total ^{39}Ar released, with only plateaux smaller than this being regarded as geologically insignificant.

All samples analysed in this study yielded reasonable plateau ages (Table 1.5-5) with three or more consecutive steps on the plateau and each comprising between 47-91% of the total ^{39}Ar released. Plateau ages were calculated in two ways. The first method weighted the steps ages according to the inverse of their variance (error) and the second weighted steps by their amount of ^{39}Ar (size). As Table 1.5-5 shows, there is a good correlation between the results by the two methods, well within the 1σ error for each of the four analyses. It is conventional to take the plateau mean age as defind by the first method as the "true" age and it is these that are quoted in the rest of the thesis.

Two isochron plots: ^{39}Ar/^{36}Ar versus ^{40}Ar/^{36}Ar and the ^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar provide an additional check on the plateau age. Both sets of isochron slope ages (Table 1.5-5) agree well with their respective mean plateau ages, again within the 1σ error limit. The intercepts of the isochron plot of the plateau steps all lie within one standard deviation of the air ratio (ca. 296) which supports the assumption that atmospheric argon is the only contaminatory argon present in the experiments.

Three specimens; metabasalt BC239 (64117), hornblende gabbro samples BC234 (64114) and AB15 (62938) show evidence of excess argon, ie. the initial steps have older $^{40}Ar^*/^{39}Ar$ ages than the main plateau age. In sample AB15 (62938) this excess argon causes the total fusion age to be some 14 my older than the plateau age. Steps affected by excess argon are not included in the plateaux. The age spectra from specimen BC239 (64117), BC133 (64116) and BC234 (64114) have all undergone at least one partial reheating/outgassing event, giving low step ages in some of the early steps. Steps affected in this way are not included in the plateau age computation. A full interpretative account of individual age spectra appears later in the thesis (see Sections 2.6.2 and 3.1.2).

1.5.5. Electron microprobe mineral analysis (EPMA).

1.5.5.1. Principles of the electron probe microanalyser.

When a finely focussed beam of electrons hits the surface of a solid material it gives rise to a primary X-ray spectrum characteristic of the material. From the wavelength and intensity of the peaks in the spectrum the elements present may be identified and their concentrations measured by comparing them with intensities from materials of known concentration. The resolution of the chemical analysis is about 1μm^3 and elements from Boron to Uranium can be detected. Two methods of detecting the X-rays are commonly exployed, the wavelength dispersive spectrometer (WDS) and the energy dispersive spectrometer (EDS). The EDS is an electronic device, employing a Li doped Si crystal and detects elements from Na to U at a detection limit of about 0.2 wt%. The device is rapid as X-rays of all energies are detected simultaneously. The WDS is a mechanical device which detects elements individually using diffraction from a crystal of known lattice spacing. It has a detection limit of about 0.002 wt% and detects elements from Boron to Uranium.

The area of analysis is located under the electron beam by observing the specimen using a light optical microscope. Rock specimens are analysed in the form of polished thin sections or slabs.

1.5.5.2. Analytical procedure.

All mineral compositions reported in the thesis were analysed by energy-dispersive microprobe at the Geology Department, Manchester University following the method of Reed and White (1975). The twenty-eight specimens analysed were polished at Liverpool and coated with a 20 nm carbon film. Individual analyses were taken on 1-2 micron spots with a counting time of a 100 seconds. Data were corrected for deadtime, background and matrix effects.

Pyroxenite samples BU417 (64159) and BU418 (64835) from the Shetland Ophiolite were analysed on a modified Cambridge Instrument Company Geoscan microprobe. This machine used only energy-dispersive spectrometer (EDS) analysis. The EDS comprises of a Kevex Detector, a Horwell 2010 pulse processor and Link Systems 290 electronics. Link Systems ZAF-4/FLS software was used to convert X-ray spectra obtained from the specimen into chemical analyses. The ZAF-4/FLS software deconvoluted overlapping x-ray peaks and subtracted background radiation by reference to a previously obtained library of standard peak profiles. X-ray intensities were automatically ZAF corrected using a procedure based on the TIM1 programme of Duncumb and Jones (1969). The atomic number correction described by Duncumb and Reed (1968) was used together with Reed's (1965) fluorescence correction. The absorption effects were calculated using Philibert's (1963) equation with σ and μ/p as calculated by Yakwitz et al., (1973).

Operating conditions: 15 kV electron beam accelerating voltage;
75 degree X-ray Take off angle;
3nA specimen current on cobalt metal and
2.5 kCPS output count rate from cobalt
with 18% detection system dead time.

All other samples were analysed on Manchester's CAMECA Camebax microprobe using a Link Systems 860-500 EDS system. A software package called "SPECTA" was used for this automated EDS system. The ZAF correction was the same as for the CIC Geoscan machine.

Operating conditions: 15 kV accelerating potential;
40 degree Take off angle and a
3 nA beam current for EDS analysis.

Principle standards used:

Element	Standard	Element	Standard
F	Fluorite	Ti	Rutile
Na	Jadeite or Albite	Mn	Tephroite
Mg	Periclase	Fe	Fayalite
Al	Corundum	Cr	Metal
Si	Wollastonite or Forsterite	Ni	
P	Apatite	Cu	
Cl	Halite	Zn	
K	Orthoclase(K-Feldspar)	Zr	
Ca	Wollastonite	Ba	Barytes

2 Ultramafites within tectonostratigraphic units of the Shetland Caledonides

The aims of this section are:

(a) to summarize the geological setting and age relations of ultramafites within metamorphic units of the Shetland Caledonides;

(b) to detail field, petrological and geochemical characteristics of the ultramafites;

(c) to discuss possible mechanisms of ultramafite emplacement and petrogenesis;

(d) to comment on the possible correlation of ultramafites within the Shetland Caledonides, and

(e) to determine, or in the case of the Shetland ophiolite to confirm, the geological provenance and tectonomagmatic affinity of the ultramafites.

2.1 Ultramafites within the Western gneisses

The Western gneisses occupy an area some 5 km x 2.5 km, in the N Roe area, at the extreme NW tip of the Shetland mainland (Figure 1,2-2). The gneisses are subdivided into two main units, the Uyea group in the W and the Wilgi Geos group in the E, which are separated by the steep, eastwards-dipping Uyea shear zone (Figure 2.2-1). The two units consist mainly of complexly foliated, quartz-feldspathic orthogneisses (orthoclase-oligoclase-quartz ± hornblende ± biotite ± epidote metamorphic assemblages), with lenses of pyroxene-hornblende granulite, sheets of mafic and ultramafic gneiss, and veined by foliated pegmatite sheets. The mafic and ultramafic gneisses include coarse- to fine-grained hornblendites and hornblende clinopyroxenites. Gneisses of the Uyea group are also cross cut by large sheets of massive metagabbro, eg. at Fugla Ness and Uyea island (Figure 2.2-1).

K-Ar hornblende radiometric dates for an early, hornblende-rich mafic intrusion from the Uyea group range between 2873 and 2661 Ma (Flinn et al., 1979) and are comparable with dates from the Pre-Scourian/Scourian-Badcallian (2900 - 2500 Ma), Archean Lewisian metamorphic basement of the Hebridean craton of NW Scotland (cf. Windley, 1982).

The Wilgi Geos group of the Western gneisses, is truncated in the E by a steep (ca. 60°), eastwards-dipping, major, ductile tectonic discontinuity - the Wester Keolka shear zone (Figure 2.2-1) - correlated by Pringle (1970) with the Moine thrust zone of NW Scotland. The Wilgi Geos group shows a late-stage (probably Caledonian) schistosity and zones of shearing, including locally developed mylonitization parallel to that in rocks E of the Wester Keolka shear zone. The Uyea group show no Caledonian reworking. Directly E of the Wester Keolka shear zone is the Sand Voe unit (Figure 1.2-2), formly the Sand Voe group of Pringle (1970). This unit consists of Moine-like quartzose psammites and pelites (commonly with a platey tectonic foliation) tectonically interleaved with slices of Lewisian inlier-like, banded and blastomylonitic hornblende-orthogneisses and ultramafites (Eastern gneisses; Figure 2.2-1).

The Western gneisses are spatially related to an area of strongly developed magnetic and Bougier anomaly systems on the continental shelf between Shetland and the W Shetland basin

(Flinn, 1969; Bott and Watt, 1970). These anomalies are considered to mark an area of basement gneisses on the shelf which may be continuous with the Hebridean craton (cf. Watson, 1984).

It is clear from the above outline description that the Western gneisses represent a foreland basement complex of Archean Lewisian gneisses and granulites exactly similar to that of NW Scotland. The foreland rocks are overridden by tectonostratigraphic units of the Caledonian province, assemblages of which include reworked Archean Lewisian-like basement with a tectonically interleaved cover-sequence of Moine-like psammites and pelites. The Western Keolka shear zone and possible the subparallel Uyea shear zone, represent northern, more ductile, probably deeper-level analogues of the orogenic front (Moine thrust zone) seen in NW Scotland. The steeper dip of the Wester Keolka shear zone, compared with the Moine thrust zone, possible reflecting a ramp geometry of the frontal tectonic discontinuity at the deeper crustal level.

N.B. The Western gneisses, with only minor, hornblende-rich, ultramafic lenses, represent a fragment of the orogenic foreland and do not strictly form part of the Caledonian orogen in Shetland, consequently they are not discussed in detail within the thesis.

2.2 Ultramafite within the Sand Voe unit

2.2.1 Geological setting

The Sand Voe unit (Flinn et al., 1979; Flinn, 1985) crops out within the N. Roe and Hillswick areas of the NW Shetland mainland (Figure 1.2-2). This complex tectonostratigraphic unit lies E of the Wester Keolka shear zone and W of the Virdibreck shear zone, and is overlain by the Dalradian-like Queyfirth unit (see section 2.9). The Sand Voe unit is composed of tectonically interleaved Lewisian inlier-like gneisses (Western gneisses (see section 2.1) and Eastern gneisses; Figure 2.2-1) and Moine-like cover rocks (Sand Voe group and Hillswick group; Figure 2.2-1). The Eastern gneisses comprise of banded-hornblendic gneisses, blastomylonitized hornblendic orthogneisses (Figure 2.2-4d) and ultramfites. The Sand Voe group is made up mostly of psammites and semipelites, with laterally persistent pelitic garnet-mica gneissose schists, especially below the Virdibreck shear zone (Figure 2.2-1). The Hillswick group is substantially similar to the Sand Voe group, but differs in that it contains graphite and pyrite rich bands (Pringle, 1970; Robinson, 1983). Both the Sand Voe and Hillswick groups have a variably developed, platey (blasto-mylonitic) foliation, which dips steeply (40° - 60°) E or SE and minor slide zones mark the junctions with the Eastern gneisses.

K-Ar radiometric dating of hornblendes and biotite from the Swinister ultramafite (Figure 2.2-1) has yielded ages between 1043 Ma and 2313 Ma, with the younger ages thought to represent partial outgassing at, or later than, 1043 Ma (Flinn et al., 1979). $^{40}Ar/^{39}Ar$ spectra from the Eastern gneisses have high-temperature steps giving similar ages (Robinson, 1983). These data support a Lewisian inlier origin for the Eastern gneisses.

A mineral whole-rock Rb-Sr isochron age of 499 ± 144 Ma for a pegmatite affected by the late tectonic foliation associated with the Wester Keolka shear indicates emplacement of the Sand Voe unit occurred at, or after, ca 499 Ma (Flinn et al., 1979).

Ultramafites within the Sand Voe unit are numerous and exposed in seven main areas (Figure 2.2-1): (a) Fethaland, GR: [HU 37 94]; (b) Sand Voe, GR: [HU 36 91]; (c) N Roe, GR: [HU 37 90]; (d) Housetter-Skelberry, GR: [HU 36 86]; (e) Colla Firth, GR: [HU 35 83]; (f) Swinister, GR: [HU 33 80]; (g) Hillswick, GR: [HU 27 76]. The ultramafites occur as minor, tectonic masses within areas of dominantly Eastern gneisses or dominantly Sand Voe group rocks.

2.2.2 Details of exposure and rock types

2.2.2.1 Fethaland area

(a) Wick of Breibister ultramafite (GR: [HU 3757 9380]): a 2.5 x 30 m. partially disrupted, tabular, concordant, massive to schistose, steatitized ultramafite body is exposed at the cliff base.

(b) Skinisfield ultramafite (GR: [HU 3775 9365]): a 50 - 60 m wide, fault-bounded, ultramafite mass, composed of phacoidal, antigorite-serpentinite slivers separated by steatitized shear zones is well exposed on the coast and lies directly below the Virdibreck shear zone.

2.2.2.2 Sand Voe area

(a) Benigarth ultramafite (GR: [HU 3670 9110]): a NNE-SSW trending, elongate (ca. 700 m long), narrow (20 - 50 m wide), strongly foliated, concordant, antigorite-serpentinite mass is exposed on the coast, with the ultramafite outcrop (defined by a > 1000 gamma positive magnetic anomaly) extending inland.

(b) Sand Voe ultramafite (GR: [HU 3610 9104]): a NNE-SSW trending, elongate (ca. 1 km long), 10 - 30 m wide, strongly foliated, antigorite-serpentinite mass is poorly exposed, but has a well-defined, linear, > 1000 - 3500 gamma, positive magnetic anomaly which is truncated by the Silver Geo and Flugarth faults.

2.2.2.3 N Roe area

(a) Faa croft ultramafite (GR: [HU 373 902]): a 10 x 60 m, tabular, concordant, ultramafite body (Figure 2.2-2a), composed of partially serpentinized, fine-scale layered, mosaic-porphyroclastic, harzburgite tectonite and granoblastic dunite tectonite (Figure 2.2-2b, c and d) is exposed E of Faa croft.

(b) Brei Geo ultramafite (GR: [HU 3790 8980]): an irregular shaped, fault-bounded, partially steatitized, antigorite-serpentinite mass is exposed S of Brei Geo and lies just below the Virdibreck shear zone.

(c) The Crub ultramafites (GR: [HU 3758 8937]): numerous, minor, steatite tectonic slivers lie within a NE-SW trend fault zone exposed along the cliff base.

2.2.2.4 Housetter - Skelberry area

(a) Houlland ultramafites (GR: [HU 3696 8713] and [HU 3675 8705]): two, elongate, NNE-SSW trending, ultramafite masses crop out at Clothie croft (not exposed) and on the NW slope of Billia Field, where serpentinized pyroxenite and antigorite-serpentinite are poorly exposed. Both masses are associated with > 2000 gamma positive magnetic anomaly systems.

(b) Skelberry ultramafite (GR: [HU 3659 8682]): a minor, tabular, concordant, serpentinized peridotite is exposed at the roadside NNW of Skelberry and lies along strike from the unexposed ultramafite at Clothie croft.

(c) Housetter ultramafites (GR: [HU 3617 8500]): five, separate, elongate, NNE-SSW trending, poorly exposed, ultramafite (serpentinized-antigorite) masses crop out NW, W and SW of the Loch of Housetter. Outcrops are defined mainly on the basis >1000 gamma positive magnetic anomaly systems.

2.2.2.5 Colla Firth area

(a) The Brig ultramafite (GR: [HU 3576 8433]): phase and modally layered serpentinized dunite, peridotite and pyroxenite, with occassional crescumulate layering, is exposed N of Saltoo pier.

(b) The Rettuvie ultramafite (GR: [HU 3767 8470]): a >7 m wide, foliated, fault-bounded, serpentinized dunite mass is exposed on the foreshore.

(c) Cleber Wick ultramafite (GR: [HU 3748 8415]): a ca. 30 m wide, complex, phacoidal, antigorite-serpentinite mass is exposed on the foreshore and as a series of isolated stacks. Junctions with the surrounding metasedimentary schists are marked by steatitized shear zones and to the W meso-scale fold interference patterns are exposed in the cliff section.

(d) Scarf Stane ultramafites (GR: [HU 3512 8340] and GR: [HU 3531 8333]): a thin, < 1 m wide, 2 - 3 m long, concordant, foliated, antigorite-serpentinite mass is exposed in the Burn of Forsa. Two minor, serpentinized dunite masses are exposed on the coast S of Scarf Stane and have faulted/sheared contacts with country-rock gneisses.

(e) N Collafirth ultramafite (GR: [HU 3517 8299]): an irregularly shaped, serpentinized dunite mass is poorly exposed SE of N Collafirth and is associated with a significant positive magnetic anomaly system extending inland.

(f) Crooksetter ultramafite (GR: [HU 3550 8293]): foliated and massive serpentinized dunite is complexly interdigitated with banded-hornblendic gneiss along the coast between Crooksetter pier and Skeo Bighta; an associated > 1000 gamma positive magnetic anomaly system extends SSW inland.

(g) Lock of Queyfirth (?)ultramafite (GR: [HU 3550 8200]): a possible serpentinized ultramafite mass is defined SE of Haa of Queyfirth by a minor, > 1000 gamma positive magnetic anomaly on the coast.

2.2.2.6 Swinister area

(a) Oxensetter ultramafites (GR: [HU 3425 8295] and GR: [HU 3409 8257]): five, minor, serpentinized dunite masses crop out in the Burn of Oxensetter section, N of Oxensetter. Exposure is poor and three of the masses are defined by magnetic anomalies alone. Three, minor, concordant, tabular, foliated, serpentinized ultramafite masses also crop out about 700 m NNE of Oxensetter.

(b) Twart Burn ultramafites (GR: [HU 3419 8190] and GR: [HU 340 817]): several, minor, ultramafite pods entirely enclosed in hornblendic gneiss are exposed 500 m SSE of Oxensetter; a serpentinized pyroxenite mass, with a well-developed > 1000 gamma positive magnetic anomaly, is exposed at Twart Burn.

(c) Orr Wick ultramafite (GR: [HU 3391 8135]): a podiform, 25 x 50 m, NW-SE trending, serpentinized peridotite mass is exposed W of Orr Wick.

(d) Swinister ultramafite (GR: [HU 337 807]): an extensive, irregularly shaped ultramfite is defined by a complex positive magnetic anomaly system around Swinister (Figure 2.2-3). The ultramafite comprises of microrhythmic, phase and modally layered (Figure 2.2-4a, b and c), serpentinized/amphibolized, peridotites and pyroxenites (Figure 2.5-5c and d) with a weakly developed penetrative tectonic foliation (Figure 2.2-4a, b and c). The ultramafite is enclosed in blastomylonitic hornblendic gneiss (Figure 2.2-4d and 2.2-5a).

2.2.2.7 Hillswick area

(a) Ber Dale ultramafites (GR: [HU 2733 7656]): several, small, concordant, steatitized ultrmafic tectonic slivers are exposed in the N cliff at Ber Dale and inland to the E (GR: [HU 2744 7653] and [HU 2767 7649]).

(b) Vida Field Stour ultramafite (GR: [HU 2765 7743]): a distinctive, coarse, granular, amphibolized (bronzite) orthopyroxenite (Figure 2.5-5) forms a large outcrop (as defined by magnetometer survey) W of Vida Field Stour.

(c) Fluga Skerry ultramafites (GR: [HU 2709 7617] and GR: [HU 2698 7604]): two, minor, concordant, steatitized ultrmafite slivers are exposed in the cliff section.

(d) Niddister ultramafite (GR: [HU 2817 7536]): a complex, podiform, ca. 20 m wide, mineralogically zoned, antigorite-serpentinite mass is well exposed in the cliff section S of Bight of Niddister. The ultramafite shows a variably developed, successive talc-carbonate, tremolite-anthophyllite and chlorite-biotite zonation.

2.2.3 Major and trace element geochemistry

Table 2.2-1 shows whole-rock major and trace element data for four ultramafites from the Swinister ultramafite (see section 2.2.2.6) and for serpentinized dunites from the Crooksetter and Brig ultramafites (see section 2.2.2.5). All five analysed rocks have high Mg′-values (81.5 - 94.3), but the group shows a wide variation in some major element abundances (eg. MgO = 27.58 - 45.41%; SiO_2 = 42.96 - 53.85%). In the Swinister ultramafites major element variations directly reflect the abundances of modal olivine, orthopyroxene and amphibole. Compatible trace element abundances are high in all the rocks analysed, but are variable (eg. Cr = 1005 - 6659 ppm; Ni = 383 - 2563 ppm) and incompatible trace element values are mostly low (eg. Sr = 3 - 23 ppm; Y = 3 - 33 ppm; TiO_2 = 0.08 - 0.22%).

2.2.4 Summary and conclusions

(a) Ultramafites within the Sand Voe unit are mostly heavily altered and variably deformed, however, possible igneous petrographic features are preserved in some ultramafites. Phase and modal layering is occassionally well displayed, with rare, modal grading and crescumulate-like features also seen (eg. Brig and Swinister ultramafites; see section 2.2.2.5 and 2.2.2.6).

(b) Major element abundances, along with high compatible trace element and low incompatible trace element values, are consistent with cumulate or restite dunitic, peridotitic and pyroxenitic protoliths and olivine ± orthopyroxene ± clinopyroxene ± chrome-spinel dominated original mineral assemblages.

(c) Radiometric data for the Swinister ultramafite (1043 - 2313 Ma) and the close spatial/structural association with Lewisian inlier-like gneisses indicate the ultramafites are Lewisian masses. Petrographically similar ultramafites are recorded from the Archean Lewisian basement of NW Scotland and these are thought to represent early, concordant, tholeiitic, layered complexes within the gneisses and granulites (Bowes et al., 1964; Davies and Watson, 1977; Savage, 1979; Windley, 1982).

(d) The Eastern gneisses, including the ultramafites, are tectonically interleaved with Moine-like cover rocks (Sand Voe and Hillswick groups) and constitute the Sand Voe unit. This unit was deformed and emplaced during Caledonian orogenesis on to the Caledonian foreland (Western gneisses) at, or after, ca. 499 Ma.

(e) Caledonian deformation and metamorphism was probably responsible for the intense schistose foliation and accompanying steatitization seen in many of the ultramafites within the Sand Voe unit. However, possible early, ductile, anhydrous, tectonite fabrics are also recorded in some ultramafites (eg. Faa croft ultramafite; see section 2.2.2.2) and may be relic pre-Caledonian tectonic fabrics.

2.3 Ultramafites within the Hascosay slide zone

2.3.1 Geological setting

The Hascosay slide is a zone of thinly banded, platey (blastomylonitic), gneissose rocks, about 0.5 to 1 km wide, which separates the Yell Sound division (Moine-like) from the Scatsta division (Dalradian-like) of the East Mainland succession on the NE coast of Yell (Figure 1.2-2 and 2.3-1). A similar zone of platey, gneissose rocks separates the same lithological rock divisions on the Shetland mainland (Figure 1.2-2). The platey zone is interpreted as a zone of high tectonic strain (ductile thrust). Structural features within the adjacent rocks are progressively obliterated and swept into parallelism in proximity to the zone. The intense, platey foliation (blastomylonitic fabric) strikes NNE-SSE, parallel to the margins of the slide zone, and has a variably developed, shallowly northward plunging linear component (Figure 2.3-1). The slide rocks consist predominantly of platey psammites, banded-hornblendic gneisses, coarse-grained leucocratic granitic and mafic gneisses and discontinuous lenses of altered-ultramafic rock.

Ultramafites within the Hascosay slide zone are exposed in four separate areas: (a) Holm of Brough, GR: [HP 5401 0405], (b) Papil Ness, GR: [HP 544 039], (c) Ness of Cullivoe, GR: [HP 553 022], and (d) Burra Ness, GR: [HU 548 948]. Figure 2.3-1 shows the location of the main ultramafic bodies within the slide zone. All the ultramafites are wrapped by the intense, platey foliation and form low-strain augens within the slide zone.

Original, pre-tectonic relations between the ultramafites and the other slide rocks are entirely destroyed.

2.3.2 Details of exposure and rock types

2.3.2.1 Holm of Brough ultramafites

Numerous, minor, biotitic- and anthophyllitic-serpentinite slivers occur at Holm of Brough, GR: [HP 5401 0405]. The largest, 0.8 x 3.0 m elongate ultramafite mass, has an homogeneous, fine-grained, non-pseudomorphic, interpenetrative (bladed-mat) textured antigorite-serpentinite core. The absence of any obvious antigorite bastites suggest the ultramafic protolith was an olivine-rich peridotite or dunite.

2.3.2.2 Papil Ness ultramafites

On the S coast of Papil Ness, three, minor, near-spherical, 2 - 3 m diameter, ultramafic bodies are exposed at GR: [HP 5443 0397], GR: [HP 5445 0396] and GR: [HP 5433 0399]. The ultramafites are mineralogically zoned, with a fine-grained, homogeneous, non-pseudomorphic, interpenetrative (bladed-mat) textured antigorite-serpentinite cores and successive concentric outer zones of talc, tremolite and chlorite.

2.3.2.3 Ness of Cullivoe ultramafites

Altered-pyroxenites crop out on the E and SE coast of Ness of Cullivoe at GR: [HP 5545 0240] and GR: [HP 5530 0225]. Four, minor (< 5 m long), massive, coarse-grained (grain size = 5 - 10 mm), anhedral-granular textured, amphibolized and serpentinized pyroxenite masses are exposed. Three of the ultramafite slivers, on the E side of the Ness of Cullivoe, lie approximately along strike from each other and were probably originally a single unit, which has since been tectonically disrupted in the blastomylonitic foliation.

2.3.2.4 Burra Ness ultramafite

On the S coast of Burra Ness at GR: [HP 5489 9486] a single, discontinuous, 0.8 x 20 m, sheet-like ultramafite mass lies concordant with the foliation of the surrounding banded-hornblendic gneiss. The ultramafite is mineralogically zoned, with a fine-grained, homogeneous, partially steatitized, antigorite-serpentinite core and concentric, marginal zones of talc, tremolite and chlorite (0 - 20 cm thick). The lack of an obvious coarse, granular, antigorite bastites texture within the antigorite-serpentinite is consistent with an olivine-rich peridotitic or dunitic protolith.

On the N coast of Burra Ness numerous, well-developed, hornblendic, mafic pods wrapped by the slide foliation occur (Figure 2.3-1).

2.3.3 Major and trace element geochemistry

Whole-rock major and trace element data for garnet amphibolite gneiss BY41 (64143) and steatitized antigorite-serpentinite BY51 (64834) from the Hascosay slide zone, at GR: [HP 5445 0396] and GR: [HU 5489 9486] respectively, are given in Table 2.2-1. The garnet-amphibolite is broadly basaltic in composition. The steatitized antigorite-serpentinite has major (eg. MgO = 31.74%; Mg'-value = 82.6; SiO_2 = 44.72%; CaO = 8.28%) and trace (eg. Cr = 4795 ppm; 2219 ppm; Zr = 13 ppm; TiO_2 = 0.12%) element abundances consistent with a cumulate or restite peridotitic protolith and an olivine ± pyroxene ± chrome-spinel original mineralogy.

2.3.4 Summary and conclusions

(a) The ultramafites within the Hascosay slide zone, although heavily altered and strongly deformed, appear to form two different lithological groups (identified on the basis of partial pseudomorphic serpentine textures and whole-rock geochemistry): altered-pyroxenites and altered-peridotites. The peridotites may be of cumulate or mantle restite origin.

(b) The Hascosay slide zone is substantially similar to other slide zones (ductile thrusts) in the Scottish Caledonides, eg. the Sgurr Bearg slide zone (Rathbone and Harris, 1979), both in the tectonic style of deformation and in the lithologies involved in the deformation.

(c) The banded-hornblendic gneisses, coarse-grained leucocratic granitic and mafic gneisses within the Hascosay slide zone are identified as possible Lewisian inlier-type gneisses included in the zone of high tectonic strain (D. Flinn and A.L. Harris pers. comm.). Any original discordance between the Archean Lewisian basement gneisses and the psammitic (Moine-like) cover rocks is completely disrupted and overprinted.

(d) The discontinuous slices of ultramafic rock within the slide zone may, on the basis of their spatial/structural association with possible Lewisian inlier-type banded-hornblendic gneisses, also represent Archean Lewisian inliers.

(e) It may be that geochemical and geochronological investigation would provide a priori evidence for these bodies being Archean Lewisian inliers. But, it should be noted that any geochemical 'fingerprinting' study would require detailed sampling of known Archean Lewisian ultramafic bodies, probably outside Shetland. Such a study is beyond the scope of this research project. Any meaningful geochronological study would be hampered by the fact that the possible Lewisian rocks are recrystallized and have been metamorphosed during their tectonic emplacement.

2.4 Ultramafites within the Yell Sound division

2.4.1 Geological setting

The Yell Sound division lies to the E of the Walls Boundary fault and forms the lowest part of the East Mainland succession (Figure 1.2-2). The division consists of a considerable thickness of pelitic and psammatic metasediments, hornblendic-gneisses and calc-silicate granulites which bear a lithological similarity to the Moine Glennfinnan Division of the Scottish Northern Highlands (A.L. Harris, pers. comm.) and may be a northern analogue of that Division. These Yell Sound division (Moine-like) rocks on Yell are separated from the Scatsta division (Dalradian-like) of the East Mainland succession by a major slide zone (Hascosay slide zone) which runs down the NE coast of Yell (see section 2.3).

Ultramafic rocks crop out at three localities within the Yell Sound division: (a) at the Holm of Copister, S Yell, GR: [HU 471 784]; (b) at Burravoe, S Yell, GR: [HU 522 794], and (c) at Gossabrough, E Yell, GR: [HU 536 830].

2.4.2 Details of exposure

2.4.2.1 Holm of Copister ultramafite

Steatite detritus on the landward foreshore of the Holm of Copister, S Yell, (Figure 1.2-2) probably indicates the presence of a metasomatized ultramafic body in the area. At present no definite exposure exists and a magnetometer survey over the area has failed to define a likely outcrop location for the source of the steatite.

2.4.2.2 Burravoe ultramafite

A single, small (1.8 m diameter), ultramafic body crops out 150 m E of Brough pier, near Burravoe at GR: [HU 522 794] (Figure 1.2-2). The ultramafic body is podiform, wrapped by the gneissose foliation of the enclosing psammitic gneiss and has an homogeneous antigorite-serpentinite core with a thin (< 5 cm thick), marginal zone of perpendicular-arranged tremolite. The serpentinized ultramafite is associated with a number of small, hornblendic, mafic and ultramafic podiform bodies in the foreshore exposure and lies approximately along strike from the Gossabrough polymict conglomerate unit, which is some 3.5 km to the NNE.

2.4.2.3 Gossabrough polymict conglomerate unit

The Gossabrough polymict comglomerate unit crops out on the southern part of the Ness of Gossabrough, E Yell, near The Muckle Head (Figure 1.2-2 and 2.4-1a). The unit extends for approximately 200 m along strike between Groti Geo and The Bottom and has a minimum thickness of about 50 m (Figure 2.4-1b). The unit comprises of rounded to subrounded, isolate, irregularly-sized clasts of mafic and ultramafic rock in a granular, often penetratively foliated (schistose), arkosic, psammite matrix (Figure 2.4-2a). Clasts range in size from very large pebbles (30 - 60 mm or -5 - -6 phi) to boulders (> 256 mm or>-8 phi) and are matrix supported (Figure 2.4-2a and b). The largest boulder-sized clast is approximately 8 m across (Figure 2.4-1b). Within the area the conglomerate clasts tend to occur in laterally discontinuous horizons subparallel to the schistosity, which may represent separate internal beds. However, sedimentary contacts above and below the clast-bearing horizons cannot be demonstrated. Likewise bedding and other sedimentary structures within the massive, arkosic psammite are not seen.

The polymictic conglomerate contains the following clast types: (a) serpentinized dunite, (b) serpentinized and amphibolized peridotite, (c) pyroxenite, (d) antigorite-serpentinite and steatite, and (e) mafic and ultramafic hornblende schists. Although it is difficult to estimate the relative proportions of the different clast types, the hornblende schists are predominant, with serpentinized and steatitized ultramafite and pyroxenite clasts forming up to 25% of the total clast population by number. However, the proportion of serpentinized and steatitized ultramafites may been underestimated due to the fact they are generally susceptible to erosion. Numerous, prolate-ellipsoidal cavities occur within the arkosic psammite (Figure 2.4-1b) and these probably contained serpentinized or steatitized ultramafite clasts rather than hornblende schist clasts.

Individual clasts tend to be texturally and compositionally homogeneous, except for some of the steatitized ultramafites which show a concentric mineralogical zonation (Figure 2.4-2d). The clasts are elongate parallel to the regionally developed mineral lineation, are flattened in the plane of the tectonic foliation of the matrix and have a mean aspect ratio of about 1:3.2:6.5. In strain shadows, adjacent to the clasts, the undeformed matrix is coarse-grained and frequently strutureless. Occasionally, chaotically orientated mesoscopic folds of the schistosity occur in the strain shadows. Some of the clasts are boudinaged and effectively extended in the plane of the schistose foliation (Figure 2.4-2c). Many of the larger clasts also show a penetrative foliation parallel to that in the enclosing psammitic matrix. Others have a penetrative foliation oblique to that of the psammitic matrix and appear to have undergone rotation during deformation (Figure 2.4-2e).

The matrix to the conglomerate shows a coarse, penetrative schistosity and is uniform in composition on a 10's cm scale. 'Gritty' horizons within the psammite tend to be less-schistose, with coarse, granular porphyroblasts and/or porphyroclasts wrapped by the weakly developed foliation (Figure 2.4-2f).

2.4.3 Petrography and mineralogy (Gossabrough polymict conglomerate unit)

2.4.3.1 Serpentinized dunite clasts

The serpentinized dunites are homogeneous, medium-grained (mean grain size = 1 - 2.5 mm), with a porphyroclastic or granoblastic tectonite texture. Olivine is completely replaced by pseudomorphic, multipartite, mesh-textured isotropic- and α-serpentine (FIgure 2.4-3d), with carbonate and magnetite. Accessory chrome-spinel is partially altered to magnetite at the margins. In a small number of serpentinized dunites a pre-serpentinization, fluidal-type porphyroclastic tectonite texture (cf. Harte, 1977 and 1983) is evident. Medium-grained (mean grain size = 1 - 2 mm) olivine crystals (now pseudomorphed) occur with 'tails' of equant, fine-grained (mean grain size ca. 0.05 mm), anhedral-granular, olivine neoblasts (now pseudomorphed) strung out in the tectonite foliation. This foliation is parallel and probably coeval to that of the enclosing psammitic matrix. Pseudomorphic serpentine mesh-textures are, in some clasts, partially overprinted by non-pseudomorphic, bladed-mat textured areas or irregular veins of γ-serpentie (?antigorite), carbonate and/or talc (Figure 2.4-3d). These late textures are similar and transitional to those of the antigorite-serpentinite clasts (see section 2.4.3.4).

2.4.3.2 Serpentinized and amphibolized peridotite clasts

Altered-peridotite clasts range up to 8 m across (Figure 2.4-1b), are melanocratic, fine- to medium-grained (grain size = 0.07 - 5 mm), homogeneous or inhomogeneous and penetratively foliated. In thin section they show fluidal-type porphyroclastic textures (cf. Harte, 1977 and 1983), with large olivine and colourless Ca-rich clinoamphibole grains wrapped by a mosaic of fine-grained (mean grain size ca. 0.05 mm), partially pseudomorphed olivine anhedra (Figure 2.4-3e). Original chrome-spinel is variably altered to chlorite and magnetite. Interlayered with the fluidal-type porphyroclastites are 'less-deformed' domains of medium-grained (mean grain size ca. 1.5 mm), anhedral-granular (coarse or ?granoblastic) olivine and pale to colourless Ca-rich clinoamphibole. In both domains olivine is partially replaced by pseudomorphic, mesh-and ribbon-textured α-serpentine (?lizardite) and magnetite. The colourless, Ca-rich clinoamphibole (Mg/(Mg + Fe) = 87.72 - 89.82; SiO_2 = 48.89 - 50.61%; Al_2O_3 = 8.03 - 9.22%; MgO = 18.82 - 21.17%; CaO = 11.62 - 12.53%; Na_2O = 1.42 - 1.72%; Cr_2O_3 = 0.42 - 0.6% (all % on an hydrous basis) is seen replacing pyroxene in places, but generally appears in textural equilibrium with olivine. The olivine is unzoned, equant, anhedral-granular and forms between 70 - 90% of the mode (Fo = 81.23 - 81.71; CaO = 0.01 - 0.06%; NiO = 0.14 - 0.56%).

2.4.3.3 Pyroxenite clasts

Rare, minor small (<10 cm across), melanocratic, fine- to medium-grained (grain size = 0.7 - 2.5 mm) hornblende orthopyroxenite (± olivine ± chrome-spinel) (Figure 2.4-3a) and hornblende-olivine orthopyroxenite (± chrome-spinel) clasts occur within the Gossabrough polymict conglomerate unit. The pyroxenite clasts have equigranular to inequigranular, subhedral- to anhedral-granular or poikilitic textures. Most clasts are homogeneous, but one example shows modal and phase layering, with ± olivine ± chrome-spinel variation and sharp phase or modal contacts (Figure 2.4-3b). Orthopyroxene and amphibole have an homogeneous crystal distribution, are equant, anhedral-subhedral, medium-sized (grain size = 0.7 - 2.5 mm) and unzoned. The orthopyroxene is bronzite (En = 80.7 - 81.8; Al_2O_3

= 1.35 - 2.27%; TiO_2 = 0.03 - 0.17%); the amphible is a pale-colourless, Ca-rich clinoamphibole (Mg/(Mg + Fe) = 85.11 - 86.7; SiO_2 = 47.26 - 49.87%; Al_2O_3 = 9.5 - 10.34%; MgO = 18.67 - 18.98%; CaO = 12.34 - 12.51%; Na_2O = 1.13 - 1.72%; Cr_2O_3 = 0.20 - 0.26%; all % on a hydrous basis). Olivine in the pyroxenite clasts is anhedral, poikilitic or intergranular to orthopyroxene and amphibole (Figure 2.4-3c), partially serpentinized and forsteritic (Fo = 79.2 - 79.6; NiO = 0.35 - 0.63%). Accessory chrome-spinel (Al_2O_3 = 45.37 - 51.43%; FeO = 21.89 - 25.78%; MgO = 9.93 - 12.99%; Cr_2O_3 = 11.74 - 17.6%) occurs as anhedral-subhedral, fine-grained (grain size ca. 0.05 mm) crystals and mutual interference grain boundaries with, or poikilitically enclosed in, orthopyroxene and amphibole.

2.4.3.4 Antigorite-serpentinite and steatite clasts

This significant group of clasts consist of various talc - carbonate - antigorite ± tremolite ± chlorite ± garnet (?hydrogrossular) ± biotite metamorphic/metasomatic assemblages. Many of the clasts show a concentric mineralogical zonation (Figure 2.4-2d), with cores of massive, antigorite-serpentinite or steatite and successive zones of talc, radially arranged tremolite ± talc and tangentially arranged chlorite and/or biotite. The zonal sequence is similar to that for other mineralogically zoned ultramafites in Shetland (see sections 2.7 and 3.2). Cores to some of the antigorite-serpentinites show relic, pseudomorphic, mesh-textured α-serpentine (?lizardite) partially overprinted by non-pseudomorphic, interpenetrative (bladed-mat) textured γ-serpentine (?antigorite) and Fe-stained carbonate. The pseudomorphic mesh-textures are similar to those of the serpentinized dunite clasts (see section 2.4.3.1) and indicate an olivine-rich peridotite or dunite protolith.

2.4.3.5 Mafic and ultramafic hornblende schist clasts

Metabasic rocks form the main clast type in the Gossabrough polymict conglomerate unit. The clasts are mafic or ultramafic and comprise of green-brown hornblende - plagioclase (andesine) - Fe-Ti oxide ± garnet ± biotite ± sphene ± quartz ± tremolite ± clinozoisite metamorphic assemblages (not necessarily equilibrium assemblages). Most clasts are granular textured (Figure 2.4-3f) or schistose and fine- to medium-grained (mean grain size = 0.2 - 3 mm).

2.4.3.6 Psammite matrix

The matrix psammites display a variably developed schistose foliation (L > S tectonite fabric) and are broadly arkosic in composition (Figure 2.4-2f). Mineralogically, they are composed of quartz - feldspar - biotite ± garnet ± kyanite metamorphic assemblages and all mineral phases tend to be elongate in the schistosity.

2.4.4 Major and trace element geochemistry (Gossabrough polymict conglomerate unit)

Table 2.2-1 shows whole-rock major and trace element data for two serpentinized ultramafite clasts, (serpentinized dunite BY29 (64158) and serpentinized/amphibolized peridotite BY31 (64120)) from the Gossabrough polymict conglomerate unit. Both rocks have highly magnesian bulk compositions (MgO = 38.3% and 31.98%; Mg′-values = 89.9 and 85.0), moderately low CaO (1.42% and 4.92%) and Al_2O_3 (3.74% and 4.91%). Compatible trace element abundances are high (eg. Cr = 3476 and 2957 ppm; Ni = 1684 and 1851 ppm; Co = 102 and 115 ppm); incompatible trace element abundances are uniformally low (eg. Zr = 9 and 14 ppm; Y = 7.3 and 8.5 ppm; TiO_2 = 0.15% and 0.29%). Ce and Nd abundances are greater than chondrite levels (Ce_N = 7.07 and 5.23; Nd_N = 6.15 and 3.35) and show moderate LREE to MREE enrichment (Ce_N/Nd_N = 1.15 and 1.56). Major and trace element values are consistent with an olivine-rich peridotitic protolith, with an original olivine ± clinopyroxene ± ?orthopyroxene ± chrome-spinel mineralogy.

2.4.5 Summary and conclusions

(a) The minor Burravoe ultramafite is petrographically and structurally similar to many of the ultramafite (antigorite-serpentinite) clasts within the Gossabrough polymict conglomerate unit. The Burravoe ultramafite lies approximately along strike from, and at a similar tectonostratigraphic level to, the Gossabrough conglomerate and may, therefore, represent a correlative of that unit.

(b) The Gossabrough polymict conglomerate unit forms an integral part of the Yell Sound division (Moine-like) metasedimentary sequence on the E side of Yell.

(c) The conglomerate is a polymict, matrix-supported, poorly-sorted unit dominated by sparse, rounded, pebble- and boulder-sized clasts of mafic and ultramafic rock in a massively bedded, arkosic matrix. Obvious sedimentary structures are not seen, but the conglomerate appears to form a laterally discontinuous, ca. 50 m wide, sedimentary unit.

(d) Mafic and ultramafic clast types are varied, but fall into several distinct petrographic classes, principally reflecting the composition of the protolith and the degree of metamorphic/metasomatic alteration of the rock. The clast types include: serpentinized dunites, serpentinized and amphibolized peridotites, pyroxenites, antigorite-serpentinites and steatites, and mafic and ultramafic hornblende schists.

(e) Clast protoliths include: dunite, peridotite (?lherzolite), hornblende-olivine orthopyroxenite, hornblende orthopyroxenite, basaltic and/or gabbroic rocks. Possible igneous poikilitic and cumulate-like textures are seen in some ultramafite clasts, along with possible cumulate phase and modal layering. Analysed peridotitic ultramafite clasts show high compatible element and low imcompatible trace element abundances suggestive of an ultramafic cumulate or mantle restite origin. Ce and Nd abundances in the peridotites suggest they are LREE-enriched relative to MREE, with overall REE abundances at greater than chondrite. These REE profile characteristics are typical of some Ophiolite complex mantle sequence lherzolites, Amphibole-bearing oceanic peridotites, Layered complexes, Appinite-type complexes, Boninites, South African peridotitic komatiites and Continental picrites (see section 4.1).

(f) The association of large, well-rounded, matrix-supported, poorly-sorted clasts with massive, arkosic, psammite is consistent with erosion of a nearby ultramafic-mafic mass and a high-energy environment of deposition. The arkose nature of the matrix and absence of obvious sedimentary contacts above and below the clast-bearing unit tends to preclude a deep-sea olistrostromal origin for the Gossabrough polymictic conglomerate. Taken together matrix and clasts suggest a nearby source region containing felsic, mafic and ultramafic units. One plausibe source could be the Archean Lewisian basement which is presumed to be present below the Moine-like Yell Sound division. This solution would point to emergence and erosion of the Archean Lewisian at the time of Yell Sound division sedimentation.

(g) The Gossabrough polymict conglomerate unit has suffered the same main (?Caledonian) tectonometamorphic episode(s) affecting the rest of the Yell Sound division. Clasts within the conglomerate are prolate ellipsoidal and coaxial with the L>S tectonite foliation of the area. Internal deformation within some ultramafite clasts produces fluidal-type porphyroclastic textures. In most ultramafite clast original/earlier non-hydrous minerals are totally replaced by pseudomorphic, α-serpentine, mesh-textures (?retrograde) and/or non-pseudomorphic, γ-serpentine (antigorite) bladed-mat textures. A significant proportion of ultramafite clasts are steatitized and show an undeformed, post-tectonic, concentric mineralogical zonation.

2.5 Ultramafites within the Walls metamorphic series

2.5.1 Geological Setting

The Walls metamorphic series forms an E-W trending tract, about 2.5 by 13 km, running along the northern part of the Walls peninsula (Figure 1.2.2.). The series is, for the most part, fault bounded at its southern edge but towards the western end is unconformably overlain by the Walls sandstone (Middle to Lower Devonian ORS) (Mykura and Phemister, 1976; Flinn, 1985). The series consists of quartzo-feldspathic gneisses, hornblendites, limestones, calc-silicates and semi-pelites (Mykura and Phemister, 1976; Frank, 1977). Minor migmatites and granitic pegmatites are also present.

K-Ar age determinations on hornblendes from the hornblendites within the series give ages ranging from 863 ± 13my to 366 ± 6my (Flinn et al., 1979). The older ages represent argon closure after an early, high-grade metamorphism more than 860my old, with younger ages corresponding to a later Caledonian overprinting.

The status of the rock series is problematical. The rocks seem to differ significantly from other major rock units on Shetland, and from the Lewisian, Moine and Dalradian successions on mainland Scotland. The series may be correlated with recently described minor anomalous lithotectonic units within the Moine outcrop of the Scottish Caledonides (Rock et al., 1984 and 1986).

2.5.2 Details of exposure

Ultramafites within the Walls metamorphic series occur at two main localities: at the NW corner of Maa Loch, Vementry [HU

298 603] and, at Neean Skerries [HU 269 595], see Figure 1.2-2. Smaller bodies also occur on the E coast of Milder Ness, Vementry [HU 292 601]

The Maa Loch ultramafite consists of five, closely spaced separate exposures with associated positive and negative magnetic anomalies (Figure 2.5-1). The magnetic anomaly pattern over the outcrop area is a simple arrangement of high amplitude 2000-3000 gamma positive anomalies centred over the actual outcrops, with negative anomalies adjacent. A negative anomaly at the latitude of Shetland is usually associated with a shallow-rooted magnetic body possessing remnant magnetisation in a direction not parallel to the Earth's inducing field. The high magnetic relief and associated positive and negative magnetic anomolies are taken to indicate that the causative serpentinized ultramafic body is restricted in depth. The steep magnetic gradients at the edge of the exposures suggests the serpentinized ultramafite is limited arealy to the observed exposure. The positive magnetic signature of the serpentinized ultramafite reflects the high proportion of magnetite in the rock.

The Maa Loch ultramafite is wrapped by the main S_1 foliation and lies approximately at the core of a large scale, tight F_2 fold (Frank, 1977). The 'country rock' hornblendic gneiss show no contact affects adjacent to the ultramafite and the margins of the body are sharp and non-transitional. The ultramafite, as defined by the magnetic anomaly system is elongate WSW-ENE parallel to the local trend of the main S_1 gneissose foliation (Figure 2.5-1).

Serpentinized ultramafic rock also forms the whole of the two most southerly (shoreward) of the Neean Skerries. The exposures are entirely surrounded by sea and the true extent of the ultramafic body, along with its immediate field relations are not discernable. The Neean Skerries body lies approximately along strike from Maa Loch body and the two may have been originally part of the same ultramafic mass.

2.5.3 Petrography and geochemistry

The Maa Loch ultramafite is peridotitic and consist mainly of serpentinized dunite and pyroxene-poor peridotite. Olivine and pyroxene in the rocks is variously pseudomorphed by serpentine, talc and minor amounts of carbonate. The alteration asemblages preserve the pre-existing ultramafite texture, and in some samples original chrome spinel is still present. Ultramafite samples immediately adjacent to the 'country rock' gneiss show a now pseudomorphed igneous-like texture with pyroxene bastites intergranular between pseudomorphic mesh-textured serpentine after medium-grained (crystal diameters 2-3mm), rounded olivine grains, eg. sample BV3 (64140). One peridotite, sample BV1 (64139), shows a discontinuous fine-scale (5-10mm wide), relic pyroxene phase layering with 'augen' of pyroxene (now γ-serpentine) suggestive of a fluidal or disrupted mosaic-porphyroclastic tectonite texture (cf. Harte, 1977 and 1983).

Serpentine textures in the Maa Loch rock vary within and between samples. Of the pseudomorphic textures, mesh textures formed at the expense of olivine are the most common and all five samples collected contain both α- (length fast) and γ-

(length slow) serpentine. The mesh rims are variously defined by isotropic or α-serpentine central partings; magnetic veins, or brown to reddish-brown rims, in which the colour is probably caused by inclusion of fine-grained iron oxides. Multipartite rims of isotropic or fibrous α- and γ-serpentine are common. Mesh cores are composed of clear featureless or isotropic serpentine. Hourglass-textures of α- or γ-serpentine also occur in three of the five samples. Other serpentine pseudomorphic textures include α-serpentine bastites replacive of pyroxene, in which relic cleavages are preserved.

Non-pseudomorphic textures range from interlocking to interpenetrating (as defined by Wicks and Whittaker, 1977) γ-serpentine. In a few places, an original mesh-texture is partially obliterated by later antigorite growth, usually through the encroachment of non-pseudomorphic serpentine from adjacent bastites.

Serpentine minerals are useful petrogenetic indicators because they preserve a variety of textures that are characteristic of certain types of alteration. Identification of serpentine minerals based on their textures is as follows. Mesh-textured α-serpentine is generally composed of lizardite and is a retrograde texture (Cressy, 1979; Wicks and Plant, 1979), whereas hourglass-textured serpentine, though it may be composed of lizardite, is mainly a prograde texture (Wicks and Plant, 1979). Non-pseudomorphic γ-serpentine is most commonly antigorite (Wicks and Plant, 1979) but may also be either lizardite or chrysotile. In most places, non-pseudomorphic serpentine is formed either by shearing during retrograde metamorphism or by recrystallization of mesh-textured serpentine during prograde metamorphism (Wicks and Whittaker, 1977).

The serpentine textures and minerology of the Maa Loch ultramafite indicate that they are initially retrograde in origin, and were formed from dunite (now mesh-textured sepentine) and peridotite (now mesh-textured serpentine and bastite). Later, recrystallization produced the hourglass and non-pseudomorphic textures in some serpentinized ultramafites.

Brucite was not identified in the serpentinized ultramafites and may indicate high CO_2 contents, which would react with brucite to form magnesite. Other secondary minerals include talc and magnetite.

The Neean Skerries ultramafite is peridotitic completely serpentinized, with a fibrous, interpenetrating (bladed-mat), non-pseudomorphic γ-serpentine texture and patches of accessory carbonate. This serpentinized ultramafite appears more recrystallized than the Maa Loch ultramafite.

Table 2.2-1 shows the analyses of serpentinized ultramafic samples from the Maa Loch ultramafite. The highly magnesium bulk composition (MgO = 43.77% and 45.4%; Mg'-values = 91.1 and 94.3), low CaO (0.27% and 0.37%), Al_2O_3 (0.41% and 0.75%) and SiO_2 (46.17% and 47.22%) seen in the serpentinized ultramafites indicates the protolith was a harzburgite or dunite. The samples contain very low abundances of incompatible trace elements and are rich in the compatible elements Ni (2109 and 2514 ppm) and Cr (2440-2476 ppm). Trace element values are consistent with an original olivine-orthopyroxene-chrome-spinel igneous mineral assemblage.

2.5.4 Conclusions

Based on field, petrographical and geochemical constraints, the following sequence of events is proposed for the genesis of the ultramafic bodies within the Walls metamorphic series.

(a) Inclusion or intrusion of the igneous textured harzburgite or dunite bodies, prior to the main gneissose foliation producing event.

(b) The rocks undergo regional metmorphism and tectonic disruption, probably concomitant with the greater than 860 Ma event. Tectonic fabrics (olivine-pyroxene mosaic-porphyroclastic texture) develop along discrete planes within the ultramafites.

(c) The rocks undergo retrograde metamorphism. Serpentinization and limited formation of talc, carbonate minerals and magnetite occur. Pseudomorphic mesh textured serpentine and bastites forms after pre-existing olivine and orthopyroxene. Magnetite replaces, or forms rims to, chrome spinel grains.

(d) The rocks are subjected to later prograde metamorphism; with a limited recrystallization of serpentine (lizardite going to antigorite) and formation of hourglass and non-pseudomorphic textures. The later prograde metamorphism possibly corresponding to a late Caledonian thermal overprinting event.

2.6 Dunrossness spilite group

2.6.1 Geological setting

The Dunrossness spilite group occupies approximately 6.75 km^2 of the Dunrossness peninsula, S Mainland of Shetland (Figure 1.2-2). The group is exposed in three main NNE-SSW trending, elongate masses. From N-S these are: Cunningsburgh, GR: [HU 425 272], Levenwick, GR: [HU 407 215] and Fitful Head, GR: [HU 343 137]. There are also a number of minor outlying exposures within the region and these include: Egiltoun, GR: [HU 3896 1775], near Scousburgh and Noup, GR: [HU 3528 1216], near Fitful Head. Large positive magnetic and gravity anomalies (McQuillan and Brooks, 1967) close to the main outcrops at Cunningsburgh and Levenwick extend a considerable distance (ca. 10 km) offshore to the E and may indicate the Dunrossness spilite group has a significant sub-Devonian ORS outcrop.

Stratigraphically, the Dunrossness spilite group forms the easternmost (youngest) member of the East Mainland succession (Flinn et al., 1972). The stratigraphic thickness of the group can only be estimated, but appears to be about 1 km. The group is part of the Clift Hills division (U. and/or M. Dalradian) which consist of about 3 km of rock and overlies the Whiteness (M. Dalradian) and Scatsta (L. Dalradian) divisions. The Whiteness and Scatsta divisions consist of some 10 km of metasediments of probable shallow-water origin, the Clift Hills division consist dominantly of quartzites and interbedded semipelitic and pelitic phyllites of turbiditic appearance (Flinn, 1967, 1985). The Dunrossness spilite group directly overlies the Dunrossness phyllitic group which is a distinctive unit comprising Al-Fe-rich, chloritoid-muscovite pelitic and semipelitic phyllites. Junctions between the two groups appear conformable, but faulted contact are seen in a number of places. Where probable sedimentary contacts are preserved, metavolcaniclastic or laminated black phyllitic metasediments (Dunrossness spilite group) are gradationally interbedded with chloritoid-muscovite pelitic and semipelitic phyllites (Dunrossness phyllitic group). The base of the Dunrossness spilite group is placed at the first appearance of the metavolcaniclastic or laminated black phyllitic metasedimentary rocks.

The Dunrossness spilite group is mostly faulted against M. Devonian (Givetian) ORS formations, but unconformable and onlapping relationships are demonstrable in many parts of the Dunrossness peninsula (Figure 1.2-2).

The Dunrossness spilite group is now defined to contain a lithological diverse assemblage of variously metamorphosed/metasomatised, igneous intrusive, volcanic, volcaniclastic and sedimentary rocks which lie stratigraphically above the Dunrossness phyllitic group. The rocks in all the outcrop areas are strikingly similar and the following lithologies occur within the group: serpentinized peridotites and pyroxenites, chlorite-magnetite schists, talc-carbonate schists (steatites), massive metabasaltic lava flows, metabasaltic pillow lavas, metadacitic lavas, veins and tuffs, metavolcaniclastites, metavolcaniclastic phyllites, black graphitic quartzites, laminated black graphite-rich semipelitic and pelitic metasedimentary phyllites, grey semipelitic and pelitic metasedimentary phyllites, quartz-plagioclase 'grits', calc-silicate bands, hornblende gabbros and hornblende diorites. Special lithological features of the group include: brecciated serpentinized peridotites, spinifex-like textured serpentinized peridotites, plagioclase-phyric metabasalts, amygdaloidal metabasalts, metadolerite sheets, laharic (mud-flow) breccias and rare, graphitic Fe-rich nodules in laminated black graphite-rich pelitic phyllites.

The majority of Dunrossness spilite group rocks are penetratively foliated, though to varying degrees. The tectonic foliation is usually subparallel to bedding, has a variably developed linear component and is generally parallel to the tectonic foliation in the local Dunrossness phyllitic group rocks. The Dunrossness spilite group appears to have suffered a similar deformation history as the rest of the Clift Hills division, East Mainland succession (cf. Flinn, 1967).

2.6.2 Age constraints

2.6.2.1 Stratigraphy

The Dunrossness spilite group is unconformably overlain by Middle Devonian (Givetian) ORS facies sediments (Allen, 1982; Flinn, 1985). The basal breccia-conglomerate units of the Devonian contain pelitic and semi-pelitic phyllite, and metvolcaniclastic phyllite clasts identical to lithologies within the Dunrossness phyllitic and spilite groups respectively. These observations indicate that the Dunrossness spilite group had undergone regional tectonometamorphism, uplift, exhumation and erosion prior to Givetian times (ca. 380 Ma; timescale of Harland et al., 1982).

The Clift Hills division, which contains the Dunrossness phylitic group, has been correlated with both the Argyll Group (M. Dalradian) (Flinn et al., 1972; Harris et al., 1975) and the Southern Highland Group (U. Dalradian) (Miller and Flinn, 1966; Flinn, 1985) of the Scottish Caledonides. The Argyll Group is of Vendian - lower Cambrian age and the Southern Highland Group is probably of lower-middle Cambrian age, as indicated by trilobite, acritach and chinotinzoan faunal assemblages (cf. Downie, 1975). Acritachs within the Tayvallich Limestone, the upper-most member of the Argyll Group in western Scotland, suggest a lower-most Cambrian age (ca. 590 Ma: timescale of Harland et al., 1982) for the Argyll Group/Southern Highland Group boundary. The Southern Highland Group is characterised by widespread though sporadic volcanic sequences (eg. Tayvallich Volcanics, Green Beds, and equivalents) which may be correlatives of the Dunrossness spilite group on Shetland.

2.6.2.2 K-Ar age data

Miller and Flinn (1966) report a series of ca. 400 Ma K-Ar muscovite ages for rocks from the Scousburgh aureole of the post- to late-tectonic Aith-Spiggie plutonic complex (see section 3.2) and the Channerwick granite. These data suggest muscovite K-Ar system closure (closure temperature ca. 350 °C; Jager, 1979) after a late recrystallization/intrusion event occurred in Early Devonian (Siegenian/Gedinnian; timescale after Harland et al., 1982) times. Consequently, the Dunrossness spilite group, which underwent polyphase regional metamorphism prior to intrusion of the Aith-Spiggie plutonic complex and Channerwick granite, must be older than about 400 Ma.

A single K-Ar whole-rock (muscovite the only K-bearing mineral) age date from the Dunrossness phyllitic group (Miller and Flinn, 1966) suggest closure of the K-Ar system in the adjacent regional metamorphic rocks occurred at approximately 430 Ma. This data confirms the Dunrossness spilite group, which appear to stratigraphically overlie the Dunrossness phyllitic group, as older than 430 Ma.

2.6.2.3 ^{40}Ar/^{39}Ar age spectra

Samples dated by the ^{40}Ar/^{39}Ar step heating method include two whole-rock metabasalts BC239 (64 117) and BC133 (64116), and a hornblende-separate from a hornblende gabbro BC234 (64114), from the Cunningsburgh area of the Dunrossness spilite group (Figure 2.6-1).

Whole-rock metabasalt BC133 (64116) is a pillow lava sample (cf. Figure 2.6-4a) from the E coast of Aith Voe, Cunningsburgh, GR: [HU 4411 2826]. Petrographically, the metabasaltic pillow lava is massive, homogeneous, fine-grained and schistose, with no relic igneous textures or minerals. Synkinematic garnet and blue-green hornblende porphyroblasts are aligned in a schistose groundmass of untwinned plagioclase (oligoclase/andesine), green-brown biotite, blue-green hornblende, garnet and Fe-Ti oxide (Figure 2.6-8a). Groundmass biotite occassionally overprints the schistosity and is also retrogressed to peninitic chlorite in places The metamorphic assemblage is characteristic of the amphibolite facies and garnet-biotite geothermometry (see section 2.6.4.3) indicates crystallization temperatures reached about 500 °C.

Whole-rock metabasalt BC239 (64117) is a massive lava sample from S of Red Stane, Cunningsburgh, GR: [HU 4295 2666]. The massive metabasaltic lava shows a relic igneous petrography; original plagioclase laths are partially pseudomorphed by granular plagioclase and epidote, with interstitial areas comprising a plagioclase - epidote - blue-green amphibole - chlorite - opaque metamorphic assemblage (not necessarily an equilibrium assemblage). The metabasalt lava appears to have equilibriated under epidote-amphibolite facies metamorphic conditions.

Hornblende gabbro BC234 (64114) comes from a small isolated, intrusive body W of Sands of Mail, Cunningsburgh, GR: [HU 4264 2780]. The hornblende gabbro has a well-displayed igneous texture and is medium-grained (mean grain size = 0.5 - 3.5 mm), homogeneous, enhedral- to subhedral-granular textured. Hornblende is tabular, enhedral to subhedral, compositionally zoned, with generally pale-brown/green cores and darker green rims. Late-acicular colourless clinoamphibole overprints some green hornblende grains along grain boundaries.

The $^{40}Ar/^{39}Ar$ step age data for whole-rock metabasaltic pillow lava BC133 (64114) are given in Table 2.6-1 and presented graphically as an age spectrum in Figure 2.6-12 (for full input data see Appendix A4). Examination of the age spectrum and the argon release pattern defines a major plateau, with nine consecutive steps on the plateau (steps 5 - 13), comprising 72.6% of the total ^{39}Ar released. The plateau gives an apparent age (weighted by %^{39}Ar) of 490 ± 6 Ma (1σ), which is in close agreement with the plateau age weighted by error (489 ± 5 Ma; Figure 2.6-1a), the ^{39}Ar/^{36}Ar v ^{40}Ar/^{36}Ar isochron age (491 ± 20 Ma; Figure 2.6-1b) and the ^{36}Ar/^{40}Ar v ^{39}Ar/^{40}Ar isochron age (486.4 ± 12.5 Ma; Figure 2.6-1c). A second, minor plateau (steps 3 and 4) gives an apparent age of about 470 Ma. Step 2 appears to be transitional between this second minor plateau and a minor argon loss event at, or younger than, about 160 Ma (step 1). The petrography of the rock suggests that K (and therefore the ^{40}Ar being analysed) may be contained in two distinct locales: (a) the main, synkinematic blue-green hornblende, plagioclase and biotite assemblage, and (b) the partially altered or recrystallized biotite. The main high-temperature sector of the age spectrum at 490 Ma is interpreted as representing argon released from the main synkinematic blue-green hornblende, and possibly plagioclase and biotite. The minor second plateau of the age spectrum can be correlated with argon released from partially altered or recrystallized biotite. The very minor mid-Mesozoic (ca. 160 Ma) 'event' does not correspond to any obvious petrographical feature, but probably represents argon loss from low-energy sites during weathering.

The ^{40}Ar/^{39}Ar step age data for whole-rock metabasaltic lava BC239 (64117) are given in Table 2.6-2 and presented graphically as an age spectrum in Figure 2.6-13 (for full input data see Appendix A4). The argon spectrum shows a complex multi-plateau argon release pattern. The principal plateau comprises of steps 8, 9 and 10 contains 47.4% of the total ^{39}Ar released and gives an apparent age of 486 ± 7 Ma (1σ). This age is in close agreement with the plateau age weighted by error (486 ± 9 Ma; Figure 2.6-13a), the ^{39}Ar/^{36}Ar v ^{40}Ar/^{36}Ar isochron age (496.8 ± 53.8 Ma; Figure 2.6 13b) and the ^{36}Ar/^{40}Ar v ^{39}Ar/^{40}Ar isochron age (488.4 ± 16 Ma; Figure 2.6-13c). Step 12 forms a second, higher temperature plateau with an apparent age of 587 ± 15 Ma. Step 11 appears to be transitional between the main plateau and the second high-temperature plateau. Steps 3 and 4 also form a minor plateau at the low-temperature end of the age spectrum and give an apparent age of about 380 Ma. Steps 5, 6 and 7 are transitional between this minor low-temperature plateau and the main plateau. Step 1 gives an anomalously old apparent age for the lowest temperature heating step and is probably an artifact of excess argon contamination of low-energy sites within the sample. The main 486 Ma age plateau is interpreted as representing the time of crystallization of the blue-green amphibole-plagioclase metamorphic assemblage. The high-temperature 587 Ma age plateau probably represents argon loss from relic igneous plagioclase in the rock. The low-temperature plateau of the age spectrum at 380 Ma is interpreted as a product of partial argon release from low-energy sites during weathering and joint formation prior to deposition of the Middle Devonian (Givetian) ORS sediments.

The ^{40}Ar/^{39}Ar step age data for a hornblende-separate sample from hornblende gabbro BC234 (64114) are given in Table 2.6-3 and presented graphically as an age spectrum in Table 2.6-14 (for full input data see Appendix A4). The age spectrum is dominantly composed of a single apparent age plateau which includes steps 6, 7 and 8 and contains 91.2% of the total ^{39}Ar released. The plateau has an apparent age (weighted by %^{39}Ar) of 462 ± 3 Ma (1σ), which is within the 1σ error limit for the plateau age weighted by error (461 ± 3 Ma; Figure 2.6-14a), the ^{39}Ar/^{36}Ar v ^{40}Ar/^{36}Ar isochron age (460.4 ± 21.8 Ma; Figure 2.6 - 14b) and the ^{36}Ar/^{40}Ar v ^{39}Ar/^{40}Ar isochron age (456.9 ± 12.6 Ma; Figure 2.6-14c). The 462 Ma plateau age is significantly younger than the ca. 490 Ma metamorphic event defined within the whole-rock metabasalt age spectra and is interpretate to represent argon closure in the hornblende-separate sample after igneous crystallization.

The whole-rock metabasalts, both contain hornblende as a principle K-bearing (and probable Ar-bearing) mineral phase, were probable metamorphosed at temperatures close to the Ar/Ar closure temperature of hornblende (ca. 500 °C) and as such the ^{40}Ar/^{39}Ar whole-rock metamorphic cooling ages probably give a reasonable estimate of the age of the peak of metamorphism. The more-complete metamorphic recrystallization and possibly higher temperature metamorphic condition experienced by metabasaltic pillow lava BC133 (64116), compared to metabasalt lava BC239 (64117), is reflected in the complete requilibration of the Ar/Ar system in the rock during the metamorphic event. The 490 Ma metamorphic event is clearly Caledonian in age and corresponds with the timing of the Grampian D_3 regional metamorphic peak in the Scottish Caledonides, which is known to be about 515 - 490 Ma (cf. Watson, 1984; Cliff, 1985; Dempster, 1985).

The 587 Ma igneous crystallization age for metabasalt lava BC239 (64117) confirms the stratigraphical correlation of the

Dunrossness spilite group with volcanic sequences in the Southern Highland Group, Grampian Highlands, which are also of probable lower Cambrian age (see section 2.6.2.1).

The 462 Ma igneous crystallization age for hornblende gabbro BC234 (64114) suggests the widespread intrusion of small hornblende gabbro-diorite masses within the Dunrossness spilite group post-dated the main Caledonian tectonometamorphic event(s).

Two post-Caledonian events are also recorded on the age spectra, with minor argon loss from low-energy sites at 380 Ma and 160 Ma. Both events are tentatively interpretated as possible weathering and/or brittle fracturing episodes related to rock exposure during mid-Devonian and mid-Mesozoic times respectively.

2.6.3 Details of exposure

2.6.3.1 Fitful Head

Dunrossness spilite group rocks are exposed in the huge W-facing cliff at Fitful Head (Figure 1.2-2). Metavolcanic rocks, dominantly metvolcaniclastites, have a steeply faulted eastern contact with Dunrossness phyllitic group rocks. The Dunrossness spilite group rocks dip steeply W and contain minor metabasaltic pillow lava units (eg. GR:[HU 344 137]) and calcareous dolomitic horizons (cf. Flinn, 1967).

2.6.3.2 Noup

About 1 km SSE of the main Dunrossness spilite group exposure at Fitful Head steatitized ultramafite crops out as a narrow (ca. 5 -10 m wide), sheet body within a steep gully W of

Noup, GR: [HU 3528 1216]. The gully, which the ultramafite body occupies, follows the line of a major, near vertical, N-S trending fault within Dunrossness phyllitic group rocks. The ultramafite is now poorly exposed some 50 m down the gully, that is about 150 m from the base of the cliff! The steatitized ultramafite consists of a talc-carbonate mylonite with a well-developed tectonite foliation subparallel to both the fault trend and the main regional foliation within the surrounding Dunrossness phyllitic group rocks.

2.6.3.3 Egiltoun

About 3.25 km SSW of Levenwick, N of the croft Blett at GR: [HU 3896 1775] talc-carbonate schist crops in a small E-W trending ditch. Contacts with nearby Dunrossness phyllitic group rocks are not exposed. The size of the steatitized ultramafite is not known, however, the lack of a distinct magnetic anomaly system over the body suggests it is small, probably < 1 m wide. The steatitized ultramafite lies along strike from the Levenwick Dunrossness spilite group outcrop and is possibly a southerly extension of that outcrop.

2.6.3.4 Levenwick area

The Dunrossness spilite group crops out in the Levenwick area as a ca. 3 km long, NNE-SSW trending, elongate mass (Figure 1.2-2 and Figure 2.6-2). Inland exposure is poor, but coastal exposure is near continuous. The Levenwick outcrop runs subparallel to the strike of the tectonic foliation in the Dunrossness phyllitic and spilite groups, and is parallel to internal bedding, where seen, in both rock groups. Contacts between the Dunrossness phyllitic and spilitic groups are gradational over a 5 - 10 m wide transition zone of interbedded metavolcaniclastic and metasedimentary phyllites. The contact is well-displayed on the coast N of Beni Taing (eg. GR: [HU 4086 2233]) and on the A970 road section at GR: [HU 4019 2000]. Minor, faulted contacts are also seen, eg. the A970 road section at GR: [HU 3993 1936]. The Dunrossness spilite group is thought to generally young eastwards in the Levenwick outcrop, but small-scale younging evidence is lacking.

On the coast N of Levenwick the Dunrossness spilite group has a faulted contact with M. Devonian (Givetian) ORS sediments; the contact shows extensive fault brecciation, shattering and minor mineralisation. However, at GR: [HU 400 196] a basal breccia-conglomerate unit of the ORS, with abundant clasts of Dunrossness phyllite, unconformably overlies the Dunrossness phyllite group which is stratigraphically below the Dunrossness spilite group. The unconformity dips about 30° E.

The main rock types of the Dunrossness spilite group in the Levenwick area are metavolcaniclastic phyllites, these pass upwards (eastwards) into massive metabasaltic lava flows and pillow lavas (eg. Geo of Serrit, GR: [HU 4085 2172]; Figure 2.6-3). Laminated black graphite-rich pelitic phyllite is exposed above the metabasaltic pillow lavas. Serpentinized ultramafite and steatitized ultramafite crops out as a discontinuous series of minor lenses within the metavolcanic rocks. A minor talcose steatitized ultramafite body is exposed on the coast at Steinfils Geo, GR: [HU 4183 2177], with a larger mass near Levenwick at GR: [HU 4079 2141] and other smaller masses to the S (eg. Clothie, GR: [HU 4041 2066] and at GR: [HU 3984 2029]).

All the lithologies have a strong penetrative foliation with a marked linear component shallowly plunging (10 - 50°) SSW. Minor, ovoid hornblende diorite masses are common, particularly in the Clothie area.

Outlying exposures of Dunrossness spilite group rocks in the Levenwick area also occur at Ness of Hoswick (Figure 2.6-2). Steatitized ultramafite, laminated black graphite-rich pelitic phyllites and heavily-altered metabasaltic rocks (eg. GR: [HU 4132 2288] are well-exposed on the coast and have late fault contacts with adjacent Dunrossness phyllite group rocks.

2.6.3.5 Cunningsburgh area

The Dunrossness spilite group in the Cunningsburgh area forms a ca. 4.5 km^2, irregularly shaped outcrop (Figure 1.2-2 and 2.6-1). Inland exposure is generally poor, but coastal exposure is good to poor. At the western margin of the Cunningsburgh outcrop Dunrossness spilite group rocks generally dip below the Dunrossness phyllitic group, ie. are, in gross stratigraphic terms, inverted. In places interdigitation of the two groups is apparent. The contact between the two groups is exposed at only two localities. (a) Burn of Voxter at GR: [HU 4329 2999], where black, graphite-rich, pelites, semipelites and graphitic quartzites (Dunrossness spilite group) show an apparent non-tectonic contact with silvery pelites and semipelites (Dunrossness phyllitic group). (b) Lamba Taing where the contact is disrupted by numerous, anastomosing, late (post-S) faults and fault-bounded slices of Dunrossness spilite group metavolcaniclastic phyllites are interdigitated with Dunrossness phyllites. One tectonic slice at the HTM on the N side of the geo N of Lamba Taing, GR: [HU 4304 2646] preserves a gradational, non-tectonic contact of the two groups over a 5 m wide transitional unit. The contact at this locality is very similar to the contact near Beni Taing, Levenwick (see section 2.6.3.3). In other areas of the Cunningsburgh outcrop the actual contact is not exposed, but can be tightly defined on the ground in numerous places.

As at Levenwick, direct younging evidence within the group is lacking. However, an isolated metabasaltic pillow within laminated black graphite-rich pelitic phyllite at Val Ayre, GR: HU 4413 2877] (Figure 2.6-6a) does show an apparent indentation of the host rock (?)bedding suggesting the rocks are locally inverted.

Internal bedding in the metavolcanic rocks is frequently hard to discern, particularly in inland exposures, but throughout the Cunningsburgh area bedding is generally parallel/subparallel to the main penetrative tectonic foliation, ie. approximately trends NE-SW. Rare, minor folds of bedding are seen in some more laminated lithologies, but show no consistent vergance. Fold axes are mostly coaxial with the variably developed linear component of the main penetrative foliation (cf. Flinn, 1967). The lineation generally plunges shallowly (<20°) to the SSW.

The Cunningsburgh outcrop of the Dunrossness spilites has a faulted eastern contact with M. Devonian (Givetian) ORS sediments. The fault is exposed at Mo Geo, E of Aith Voe, GR: [HU 4416 2829] and forms a 5 - 10 m wide tectonic melange with phacoidal blocks of metavolcanic phyllite, quartzite, ORS sandstones and breccio-conglomerate and black graphite-rich pelitic phyllite, along with mylonitized versions of these lithologies. Adjacent to the fault ORS sandstones and Dunrossness spilite group metasediments are cut by anastomosing, minor-fault arrays and mylonitic bands. The fault is continuous with, and probable extension of, the basal dislocation of the Quarff tectonic melange (see section 2.11) and was reactivated after deposition of the ORS.

Ultramafites are widespread within the Cunningsburgh area. The most important ultramafite unit crops out W of the main A970 road as a NNE-SSW trending, 1.25 km^2 mass. Another smaller mass occurs to the E at GR: [HU 4265 2725] and is entirely enclosed by metavolcanics. Numerous other minor exposures crop out, for example: on the N coast of Aith Voe (eg. GR: [HU 4404 2901]) W of Cunningsburgh village (eg. GR: [HU 428 291], S and E of Knowe of Wilga (eg. GR: [HU 4332 2658]) where isolated ultramafite masses occur wholely within the Dunrossness phyllitic group.

The ultramafite masses dominantly consist of foliated or massive antigorite-serpentinite and foliated or massive talc-carbonate schists (steatites). Contacts with other units of the Dunrossness spilites and the Dunrossness phyllite group are rarely seen and are everywhere marked by steatitization. Structural relationships between the ultramafites and other lithologies are unclear and the ultramafites may represent fault-bounded slices where interlayered with metavolcaniclastic phyllites and metabasaltic lavas.

The most interesting features of the ultramafites are limited to the main ultramafite outcrop. Massive, non-foliated, serpentinized ultramafite, with an orange-brown weathered surface, crops out as a unit from Burn of Gatpund, GR: [HU 4240 2706] to Vestinore, GR: [HU 4268 2800]. Within this unit occur numerous separate outcrops of an unusual serpentinized ultramafite (eg. GR: [HU 4250 2725]), with closely packed serpentine pseudomorphs of tabular, parallel-sided, elongate olivine grains upto 15 mm long and 2 mm thick, but mostly smaller. In places the elongate olivine pseudomorphs are randomly arranged (Figure 2.6-9b), but also occur as closely spaced, subparallel arrays. Some exposures show a vague layering of grain-size and orientation, with layers exhibiting elongate growth of olivine along a preferred orientation direction perpendicular or imbricated to the plane of the layering and other layers with randomly arranged, elongate olivine pseudomorphs (Figure 2.6-9a). Massive, serpentinized ultramafite with elongate olivine pseudomorphs (spinifex-like texture) pass gradationally over a distance of m's into massive, anhedral- to subhedral-granular textured, serpentinized ultramafite.

Within the same structural unit isolated outcrops of blocky, brecciated, serpentinized ultramafite occur, eg. GR: [HU 426 275] (relationships with the non-brecciated serpentinized ultramfites are not seen). The breccia is matrix-poor and comprises angular to placoidal, variably sized blocks of ultramafite (Figure 2.6-10a and d). Elongate olivine pseudomorphs are limited to the blocks (Figure 2.6-10b and d); the matrix consist wholly of serpentine and is only weakly foliated (Figure 2.6-10d). Some exposures show a vague alignment of blocks, but most show no preferred orientation of blocks.

Steatites are widespread throughout the various ultramafite outcrops in the Cunningsburgh area (Figure 2.6-1) and may be schistose, with complete destruction of earlier fabrics and petrography, or massive, with occassional relic elongate olivine pseudomorphs (Figure 2.6-9c) and brecciation (Figure 2.6-10c) seen. Most steatites have aproximately equal proportions of talc to carbonate. The majority of serpentinized ultramafites are also partially steatitized. Lenses of chlorite-magnetite schist occur in some strongly foliated steatites and may represent included and metasomatised fragments of metavolcanic rock.

Metasedimentary phyllite units comprising black-grey, closely laminated, occassionally graphite-rich, pelites and semipelites (Figure 2.6-6d) and graphitic quartzites are numerous within the Cunningsburgh area (Figure 2.6-1). Outcrops occur, for example: on the coast of Aith Voe; at Val Ayre, GR: [HU 4413 2827]); on the coast S of Sands of Mail at GR: [HU 4282 2769], and Burn of Voxter, NNE of Cunningsburgh, GR: [HU 433 297]. Bedding within the metasedimentary phyllites is defined by gross compositional differences and is generally subparallel to the colour lamination. In some units laminated black pelitic and semipelitic phyllites are interbedded with metavolcaniclastic phyllites. Isolated, small, graphitic, Fe-rich nodules elongate in the foliation (Figure 2.6-6b) and isolated, metabasaltic pillows or lava tubes (Figure 2.6-6a) also occur within finely laminated black pelitic phyllite. S of

Sands of Mail the pelitic phyllites show a strong L > S tectonite foliation (Figure 2.6-6c) and minor, coarse chloritoid porphyroblast-bearing horizons are also seen (eg. GR: [HU 4289 2769]).

The principal metavolcanic succession within the Cunningsburgh area comprises two units: a heterogeneous, metavolcaniclastic and massive metabasaltic lava dominated unit, and a metabasaltic pillow lava dominated unit.

The mixed metavolcaniclastite - massive metabasaltic lava unit occurs interlayered with steatitized and serpentinized ultramafites in the western half of the Cunningsburgh outcrop. The eastern margin of the unit occurs approximately at S Voxter, where metabasaltic pillow lavas appear in the succession. Metavolcaniclastic rocks comprise about 70% of the unit, are heterogeneous and include probable epiclastic and autoclastic lithologies. Coarse, variably foliated, metavolcaniclastic breccias are common and S of Catpund have the appearance of vesicular flow tops, where a rubbly, cariously weathered surfaces are developed (Figure 2.6-5a). Some of these represent autoclastic flow-top breccias and others are probable epiclastic lahars. The laharic breccias are very-poorly sorted and metabasaltic clasts are dominant (Figure 2.6-5b and c), however, other lithic clasts also occur and include: rare, hornblende gabbro clasts (eg. GR: [HU 4284 2783]); metasedimentary (?rip-up) clasts (Figure 2.6-7b) ; and rare, 'tear-drop' shaped, metadacite lapilli (Figure 2.6-7b). Numerous other varieties of fine- to medium-grained, bedded metavolcaniclastites and metavolcaniclastic phyllites, of tuff and lapilli-tuff appearance (though may not be pyroclastic) occur throughout the hetergeneous unit (eg. Figure 2.6-5d). Definite pyroclastic rocks have not been identified, hindered mainly by the deformed state of the rocks and their unhelpful weathering characteristics. The rare, metadacitic lapilli within some laharic breccia (Figure 2.6-7b) are the only clear candidates for pyroclastic fragments and even here the clasts may represent material brought into the volcanic environment by epiclastic processes. Massive, generally poorly foliated, <10 m thick, dark-grey, metabasaltic lavas comprise approximately 30% of the mixed metavolcaniclastite - massive metabasaltic lava unit. Amygdaloidal metabasalts (eg. GR: [HU 4346 2960]) and plagioclast-phryic metabasalts (eg. GR: [HU 4284 2705]; cf. Figure 2.6-7c) also occur within the unit. Interbedded with the massive metabasaltic lavas and metavolcaniclastites are rare quartz-plagioclase 'gritty' psammites, calc-silicate lenses (eg. GR: [HU 4256 2812]) and metadacitic lavas, veins and tuffs (eg. GR: [HU 4281 2719]).

The metabasaltic pillow lava unit crops out to the E of the mixed metavolcaniclastite - massive metabasaltic lava unit and is best displayed on the E and W side of Aith Voe (eg. GR:[HU 4410 2826]). Within the unit metabasaltic pillow lavas comprise between 30-80% of the sequence and are interbedded with massive metabasaltic lavas and metavolcaniclastites identical in appearance to those in the W metavolcanic unit. The metabasaltic pillow lavas are pale- to medium-grey, aphyric and variably deformed; pillows are closely fitted, small, flattened and elongate parallel to the foliation, and frequently show a concentric, marginal arrangement of amygdales and pale rims (Figure 2.6-4a and b). Inter-pillow areas comprised a blocky, metabasaltic breccia and/or quartz-epidote ± carbonate 'vein-like' material (Fiure 2.6-4a); the latter is readily distinguishable in the field. The large scale morphology of the pillow lavas (eg. lava tubes, etc) and clear younging relations have not been observed.

Hornblende gabbro and diorite intrusive masses are numerous and widespread within the Dunrossness spilite group outcrop of the Cunningsburgh area and occur as isolated, minor, circular or elliptical, upstanding outcrops (knolls). Fine-grained, metadoleritic chill zones are occassionally seen at the margins of some massive hornblende gabbro/diorite intrusions (eg. GR: [HU 4269 2780]). Porphyritic and pegmatitic varieties of the hornblende gabbro/diorite are also found, along with irregular, biotite - K-feldspar-rich dioritic 'clots' (eg. GR: [HU 4411 2936]). Although the intrusive masses are mineralogically relatively uniform (hornblende - plagioclase ± biotite ± K-feldspar ± Fe-Ti oxide) they can be subdivided, on a structural basis, into foliated and non-foliated varieties (possibly a pre-and post-tectonic suite).

One of the non-foliated hornblende gabbros gives a $^{40}Ar/^{39}Ar$ hornblende age which clearly post-dates the presumed peak of metamorphism (see section 2.6.2). It is therefore probably correct to regard at least some of the non-foliated hornblende gabbro/diorites as not being an integral part of the Dunrossness spilite group.

2.6.4 Petrography

2.6.4.1 Serpentinized ultramafites and steatites

Textures in the serpentinized ultramafites are variable. They can be subdivided into four main lithological types, based on the presence and form of early relic textures, and the style and degree of non-pseudomorphic replacement features: (a) massive serpentinized peridotite, (b) spinifex-like textured serpentinized peridotite, (c) serpentinized pyroxenite and (d) undifferentiated antigorite-serpentinite. The *massive and* spinifex-like textured serpentinized peridotites are best displayed in a structural unit between Burn of Catpund and Vestinore in the Cunningsburgh area (see section 2.6.3.5). Serpentinized pyroxenite is known from only one isolated, small locality W of Cunningsburgh village (see section 2.6.3.5). Undifferentiated antigorite-serpentinites are widespread throughout the Dunrossness spilite group outcrops and comprise the dominant serpentinized ultramafite rock type.

(a) The massive serpentinized peridotites have a medium-grained (mean grain size = 1 - 3 mm), uniform, equigranular, massive, anhedral-to subhedral-granular texture of cumulate appearance (Figure 2.6-11a). Pseudomorphed olivine and ?chrome-spinel can show mutual interference grain boundaries but in places separate grains appear to merely touch (Figure 2.6-11a). Olivine forms > 80% of the massive serpentinized peridotites and shows no mineral lamination or layering. Individual olivine grains are anhedral to subhedral, equant to tabular, solid ie. show no obvious skeletal or embayed morphology and are wholly pseudomorphed by multipartite, mesh-textured γ-serpentine and iddingsite (Figure 2.6-11a). Opaque ore grains (former chrome-spinel) are mostly medium- to coarse-grained (grain size = 0.5 - 3 mm), anhedral, equant and are magnetite occassionally with Cr-rich chlorite rims (eg. Figure 2.6-11b).

(b) The spinifex-like textured serpentinized peridotites are generally medium- to coarse-grained, can be homogeneous or inhomogeneous, with elongate olivine pseudomorphs randomly arranged (Figure 2.6-9b and 2.6-11d) or as closely packed, subparallel arrays with a perpendicular or imbricate alignment to textural/grain size layering (Figure 2.6-9a). Layering is rare and intermittant within the spinifex-like textured serpentinized peridotites and is laterally discontinuous with thin (< 10 cm thick), concordant layers and sharp textural/grain -size contacts. The elongate olivine pseudomorphs in the spinifex-like rock are enhedral, tabular, parallel sided and where randomly orientated appear mostly to cut straight across other elongate olivine pseudomorphs (Figure 2.6-11c). However, in some cross-cutting relationships one or both elongate olivine pseudomorphs may 'neck' or develop enhedral terminations at the crossing point. Elongate olivine pseudomorphs invariably show well-defined grain boundaries and no skeletal or embayment features, although the internal, radiate, bladed γ-serpentine texture (Figure 2.6-11d) is generally too coarse to preserve any fine morphological detail. Intergranular areas are composed of carbonate ± talc ± magnetite, with a fine-grained, granular, non-pseudomorphic texture.

Massive and spinifex-like textured serpentinized peridotites in the Cunningsburgh area are in places brecciated (see section 2.6.3.5). The breccia matrix in thin section comprises fine-grained, granular, interpenetrative (bladed-mat) textured γ-serpentine (antigorite) and magnetite, with a finely laminated foliation defined by magnetite stringers which wrap fragments of massive and spinifex-like textured serpentinized peridotite.

(c) The serpentinized pyroxenite has a uniform equigranular, medium- to coarse-grained (mean grain size = 6 mm), anhedral-granular, cumulate-like texture, with original pyroxenes pseudomorphed by crude interlocking, γ-serpentine/tremolite bastites and accessory talc and carbonate.

(d) Massive and spinifex-like textured serpentinized peridotites with relic, early textures are locally seen to be overprinted by non-pseudomorphic schistose and massive, interpenetrative (bladed-mat), γ-serpentine (antigorite) textures. These antigorite-serpentinites usually contain minor talc and carbonate, (ie. are partially steatitized) and within individual outcrops can be seen to pass into massive, or schistose steatite (talc-carbonate schists).

In a few localities, steatites crudely mimic earlier spinifex-like serpentinized peridotite petrography (Figure 2.6-9c), but most steatites are massive granular or schistose, with talc - magnesite - magnetite ± calcite ± chlorite ± γ-serpentine ± quartz assemblages.

2.6.4.2 Other lithological units

(a) Metabasaltic pillow lavas and massive metabasaltic lavas show broadly similar petrographical features and are mostly, massive, homogeneous, fine-grained, with a variably developed penetrative foliation. Occassional relic igneous or spilitic features are seen, and include: carbonate-filled amygdales (Figure 2.6-8c); amygdales (or perhaps spheriolites) pseudomorphed by granular, epidote and chlorite (Figure 2.6-4c); albite phenocrysts in some massive metabasaltic lavas (Figure 2.6-7c); relic subophitic , igneous, groundmass textures (Figure 2.6-4c), and early (?pre-metamorphic), spilitic albite ± epidotite ± chlorite ± carbonate mineral assemblages. Syn-kinematic, metamorphic assemblages include: blue-green hornblende - epidote - plagioclase (albite - oligoclase) - Fe-Ti oxide ± chlorite ± clinozoisite ± biotite ± actinolite ± garnet ± carbonate ± sphene (Figure 2.6.4d, 2.6-7c and 2.6-8a). Late, post-kinematic, blue-green hornblende (Figure 2.6-8 and c), biotite and chlorite porphyroblasts occur in some metabasalts. Metabasaltic pillow lavas are generally less-mafic than the massive metabasaltic lavas (compare Figure 2.6-4d with the ground mass in Figure 2.6-7c).

(b) Rare, metadacitic lavas, veins and tuffs occur throughout the Dunrossness spilite group. Presumed metadacitic tuffs are thinly interbedded with more mafic metavolcaniclastic phyllites and metadacitic lapilli also occur with some metavolcaniclastic, laharic breccias (Figure 2.6-7a and b). The metadacites are petrographically very distinctive, comprising almost wholly of ?flow-aligned, small, albite laths, accompanined by chlorite, carbonate and Fe-Ti oxides, and patchily overprinted by epidote-dominated metamorphic assemblages (Figure 2.6-7a).

(c) Black-grey, occassionally graphitic, metasedimentary phyllites are widely distributed within the Dunrossness spilite group and tend to be finely laminated. In some samples the lamination is clearly a locally developed tectonic, crenulation cleavage (Figure 2.6-8e). The majority of the black-grey, metasedimentary phyllites are pelitic or semipelitic in composition and comprise quartz - feldspar - epidote - biotite - opaque ore ± muscovite ± chlorite ± actinolite ± garnet ± chloritoid (Figure 2.6-8b) metamorphic assemblages. Interbedded with the pelites and semipelites are laminated, graphitic quartzites (Figure 2.6-8d) which may represent recrystallized cherts.

(d) Rare calcareous and psammitic metasedimentary rocks also occur in the Dunrossness spilite group and include: calc-silicate layers (carbonate - biotite - garnet; Figure 2.6-7d); dolomitic crystalline limestone, and quartz - plagioclase 'gritty' psammites.

(e) Metavolcaniclastites and metavolcaniclastic phyllites are common and extremely heterogeneous. In thin section the rocks show metamorphic mineral assemblages similar to the metabasalts, but are generally more schistose, with many showing relic lithic clasts. Other metavolcaniclastites bear mineral assemblages transitional between the metabasalts and the laminated black-grey graphite-rich pelitic and semipelitic phyllites and appear to be an admixture of pelagic/clastic and volcanogenic sediment. The laharic breccias occassionally show a similar mixture with a black, pelitic matrix and coarse, dominantly metabasaltic, lithic clasts (Figure 2.6-7a).

2.6.4.3 Garnet - biotite geothermometry

Garnet - biotite pairs from the Cunningsburgh metabasaltic pillow lava BC133 (64116) were analysed (see Table 2.6-7) by microprobe and four methods for determining the temperature of crystallization applied: (a) Goldman and Albee (1977); (b) Ferry and Spears (1978); (c) Thompson (1976), and (d) Penchuk (1970). The four methods used involved differing calibration techniques in the original study and therefore often produce different temperature estimates for the same garnet - biotite analyses.

Goldman and Albee's thermodynamic equation, $24\ln K_D = -\Delta G^{\circ}/RT$, was derived using a calibration of garnet - biotite pairs against O^{18}/O^{16} in thirteen selected samples. Temperature estimates using this equation are significantly lower than for the other thermometers used (see Table 2.6-8). This is probably due to two principle factors: (a) that elemental and isotopic partitioning do not have the same temperature dependency, and (b) the O^{18}/O^{16} calibration used was low due to isotopic requilibration at decreasing temperatures in the selected rock samples.

Ferry and Spears (1978) derived their thermodynamic equations from observed elemental partitioning between garnet and biotite under experimental conditions. The equation $\ln K_D = -2109/T_K + 0.782$, is used in this study to give an estimate of temperature. This thermometer takes no account of the necessary corrections for Ca and Mn in garnet and Al^{vi}, Fe^{+++} and Ti in biotite. Ferry and Spears (1978), stated that their equation is valid if the ratio (Ca + Mn/(Ca + Mn + Mg + Fe) in the garnet does not exceed 0.2 and the ratio $(Al^{vi} + Ti)/(Al^{vi} + Ti + Fe$

+Mg) in the biotite does not exceed 0.15. Unfortunately, these ratios in BC133 garnets and biotites are higher than the limits of Ferry and Spears (1978) and this probably accounts for the variance of temperature estimates using this equation compared to the other thermometers used (Table 2.6-8).

The third garnet - biotite thermometer used (Perchuk, 1970) was calibrated against amphibole - plagioclase and garnet - amphibole pairs from natural rock samples. Results using Perchuk's thermometer are consistently high relative to the other thermometers used (see Table 2.6-8). This is primarily due to error in Perchuk's original calibration technique. The calibration used is dependent on: (a) the accuracy of garnet - amphibole thermometry for the selected samples, uncertainties in the 'control' thermometer will have been passed on in the garnet - biotite temperature equations; and (b) the accuracy of garnet - biotite analyses, garnet and biotite data used in some sections of Perchuk's study were analyses of mineral separates rather than probe analyses and therefore may be erroneous due to mineral zoning, inclusions, etc.

Thompson's thermometer used analyses of coexisting garnet - biotite and garnet - cordierite in rocks where the temperature of crystallization had already been determined using a petrogenetic grid (mica - feldspar - Al_2SiO_5 - quartz phase relations). The Thompson (1976) calibration is widely believed to give the most accurate temperature estimates, as it allows for the type of assemblage coexisting with the garnet - biotite and is based on high quality analyses of natural mineral pairs.

Temperature estimates are obtained under the equation: $10^4/TK = (\ln K_D + 1.623)/0.2825$

From Table 2.6-8 it is clear that there is a temperature difference between garnet rims and cores. This is due to a 'normal' zonation in the garnet porphyroblasts. The zonation reflects continued garnet growth during declining metamorphic temperatures. Coexisting biotites show no similar zonation and are believed to have undergone recrystallization and requilibration in the later stages of metamorphism. From these observations it is assumed that only the garnet rims are likely to be in equilibrium with the adjacent matrix biotite and that these mineral pairs give a temperature estimate of the late-stage metamorphic conditions of about 497 °C.

2.6.5 Major and trace element geochemistry

2.6.5.1 Serpentinized ultramafites and steatites

Whole-rock major and trace element data for serpentinized ultramafites from the Dunrossness spilite group is given in Table 2.6-4 and is plotted against the fractionation index $100Mg/(Mg + Fe^{2+})$ in Figure 2.6-15, 16 and 17.

Serpentinized peridotites from both the main Dunrossness spilite group outcrops, at Cunningsburgh and Levenwick, show no compositional differences. Similarly, serpentinized peridotites with or without spinifex-like textures have the same major and trace element compositions. The serpentinized peridotites have uniformally high-magnesian bulk compositions, with high MgO (36.59 - 48.13%) and high Mg'-values (90.6 - 93.2). CaO abundances are generally low, with moderate variation. (0.04 -

4.25%). The serpentinized peridotites are relatively poor in Al_2O_3 (0.52 - 1.56%), SiO_2 (42.85 - 49.63%), extremely poor most other major elements and show a moderate major element variation within the sample suite. Compatible trace element abundances in the serpentinized peridotites are variable, but are generally high (eg. Cr = 1833 - 4198 ppm; Ni = 1631 - 2350 ppm; Co = 72 - 113 ppm). Incompatible high field strength (HFS) and large lithophile (LIL) trace element abundances are all uniformly very low (eg. Y = 1 - 4 ppm; V = 16 - 39 ppm; TiO_2 = 0.01 - 0.10%; Zr = 2 - 19 ppm; Sr = 1 - 30 ppm) throughout the serpentinized peridotites.

The serpentinized pyroxenite BC41 (64113) shows major element features distinct from the serpentinized peridotites and has lower MgO (21.59%), Mg′-value (84.0) and significantly higher SiO_2 (55.36%), Al_2O_3 (5.55%) and CaO (8.41%). The serpentinized pyroxenite has compatible and incompatible trace element abundances comparable with the other serpentinized ultramafites (eg. Cr = 2352 ppm; Ni = 1971 ppm; Co = 106 ppm; Y = 13 ppm; TiO_2 = 0.09%; Zr = 3 ppm; Sr = 9 ppm). However, the Sc value is slightly higher (16 ppm) and is consistent with a fact that Sc is incompatible with olivine, but compatible with pyroxene, particularly Ca-rich clinopyroxene.

Whole-rock major and trace element data for steatites from the Dunrossness spilite group is given in Table 2.6-4 and is plotted against the fractionation index $100Mg/(Mg + Fe^{++})$ in Figure 2.6-15, 16 and 17).

The steatite samples analysed come mostly from the Cunningsburgh area, with one sample, HOS2, from Hoswick Ness, near Levenwick and another, BFH1 (64141), from the Noup steatitized ultramafic mass, near Fitful Head (see section 2.6.3). In general, the steatites have major and trace element characteristics (on a volatite free basis) exactly similar to the serpentinized ultramafites, particularly the serpentinized peridotites. Mg′-values (86.1 - 93.3) and compatible trace elements (eg. Cr = 2091 - 3789 ppm; Ni = 1540 - 3514 ppm; Co = 80 - 42 ppm) are substantially the same. Also, the majority of incompatible trace element abundances (eg. Y = 1 - 8 ppm; V = 17 - 60 ppm; Zr = 2 - 17 ppm) are generally the same. However, the steatites do show a number of notable geochemical differences to the serpentinized ultramafites and in particular the serpentinized peridotites. The steatites show a greater variation in MgO (21.98 - 46.46%), CaO (0.28 - 15.3%), SiO_2 (34.12 - 53.46%) and Al_2O_3 (0.28 - 14.64%) and some trace elements, for example TiO_2 (0.09 - 0.57%) and Sr (1 - 322 ppm). The variability of these elements is probably the result of selected elemental mobility and fractionation during steatitization, but variation due to differences in protolith character cannot be totally excluded.

2.6.5.2 Metabasalts, metadacites and hornblende gabbros

Whole-rock major and trace element data for the massive metabasaltic lavas is given in Table 2.6-4 and is plotted against the fractionation index 100Mg/(Mg + Fe^{2+}) in Figure 2.6-15, 16 and 17.

The massive metabasaltic lavas are readily distinguished from the metabasaltic pillow lavas on the basis of major elements alone. The massive lavas show significantly higher

Mg′-values (43.9 - 64.6), MgO (7.23 - 9.50%) and generally lower Al_2O_3 (13.97 - 16.49%), Na_2O (0.33 - 2.34%) than the pillow lavas. However, the two suites do appear to define a single major element variation trend in Figure 2.6-15. MgO and CaO show a positive correlation with Mg′-value and suggest differentiation involved limited mafic mineral (eg. olivine and pyroxene) fractional crystallization. The uniform Al_2O abundances suggest plagioclase was not a fractionating phase.

Compatible trace element abundances in massive metabasaltic lavas show moderate variation (Ni = 42 - 251 ppm; Cr = 29 - 315 ppm; Co = 55 - 83 ppm), are generally low, define reasonable linear variation trends and show uniformally very low Ni and a reduction in Cr and Co abundances in more-evolved members of the suite. These features, again, point to differentiation controlled by mafic mineral (?clinopyroxene) fractional crystallization. However, unlike the major element variation trends the compatible trace element trends in the massive metabasaltic lavas are not continuous with the metabasaltic pillow lavas. This effectively precludes the two metabasaltic suites from being petrogenetically related by high-level fractional crystallization processes.

Incompatible trace element abundances are variable in the massive metabasaltic lavas, (eg. Sr = 31 - 304 ppm; Ba = 82 - 140 ppm; Rb = 0.3 - 44 ppm; Zr = 107 - 144 ppm; Y = 28 - 49 ppm; TiO_2 = 1.74 - 2.64%; V = 336 - 490 ppm) and define generally poor fractionation trends within Figure 2.6-17. V, Y, Ti and Zr abundances show steep linear increases with differentiation and suggest an absence of Fe-Ti oxide and zircon fractional crystallization. As with the compatible trace elements, plausible fractional crsytallization trends linking the massive metabasaltic lavas and the metabasaltic pillow lavas are not seen in the incompatible trace element data.

The major and trace element data for the metabasaltic pillow lavas is given in Table 2.6-4 and is plotted against the fractionation index 100Mg/(Mg + Fe^{2+}) in Figure 2.6-15, 16 and 17.

The metabasaltic pillow lavas *all have* SiO_2 contents less than 53% and are therefore *confirmed as basaltic*. The pillow lavas show a very limited variation in major element abundances (MgO = 1.78 - 3.02%; FeO* = 12.26 - 16.35%; Al_2O_3 = 18.15 - 20.7%; SiO_2 = 46.62 - 50.95%) and Mg′-values (20.3 - 26.4). However, CaO (2.58 - 11.17%) and Na_2O (1.96 - 6.36%) do show very great variation and is probably the product of varying degrees of spilitization in the pillow lavas. The most distinctive major element features, compared with the massive metabasaltic lavas, are probably the low MgO and high Al_2O_3 contents in the metabasaltic pillow lavas.

Compatible trace element abundances in the metabasaltic pillow lavas are generally high (eg. Cr = 171 - 784ppm; Ni = 89 - 326 ppm; Co = 47 - 111 ppm) and suggest the metabasalts are primitive. However, this is contradicted by the low Mg -values. In Figure 2.6-16 the metabasaltic pillow lavas do not lie on an extension of the fractionation trend defined by the massive metabasaltic lava data.

Incompatible trace element abundances in the metabasaltic pillow lavas are comparatively low for rocks with low Mg'-values. Rb (10 - 26 ppm), Zr (137 - 216 ppm), Nb (8 - 10 ppm), Y (27 - 53 ppm), TiO_2 (1.25 - 1.76%) and V (173 - 255 ppm) show limited variation within the suite. In contrast, Sr (110 - 310 ppm) and Ba (123 - 414 ppm) show a moderate dispersion probably due to variable secondary mobility of these elements during spilitization and/or regional metamorphism.

Whole-rock major and trace element data for the metadacite lava 68143 and hornblende gabbros from the Dunrossness spilite group is given in Table 2.6-4 and is plotted against the fractionation index 100Mg/(Mg + Fe^{2+}) in Figure 2.6-15, 16 and 17.

The metadacite lies, for most major and trace elements, well off the variation trends defined by the metabasaltic rocks. Petrogenetic modelling of the dacite magma has failed to find any reasonable crystal-liquid fractionation hypothesis which could link the metadacite and metabasaltic rocks. Hornblende gabbros from the Dunrossness spilite group show major and trace element similarities with the massive metabasaltic lavas and, therefore, may represent more-slowly cooled, higher-pH_2O magma bodies of broadly similar composition to the massive metabasaltic lavas.

2.6.5.3 Basalt magma type

The metavolcanic rocks of the Dunrossness spilite group have been metamorphosed to the amphibolite-facies assemblages during regional metamorphism (see section 2.6.4.2 and 2.6.4.3). As even low-grade metamorphism may cause changes in the bulk major element geochemistry of basalts (eg. Hart et al., 1974; Humphris and Thompson, 1978) the use of major elements in characterizing the magma type of the metavolcanic suite is likely to be unreliable.

The plot of total alkalis (Na_2O + K_2O) against SiO_2 (Figure 2.6-18a) shows that the Dunrossness spilite group metabasalts are on the whole, mildly alkaline, though a significant number of the analysed rocks fall in the subalkaline field. Most of the rocks also lie in either the tholeiitic or alkaline field on an AFM (Na_2O + K_2O - FeO - MgO) diagram (not shown here). Unfortunately, because the basalts are metamorphosed both these diagrams cannot be relied upon to correctly describe the magmatic affinity of the metabasalts.

The classification of volcanic rocks on the basis of normative mineralogy also becomes increasingly difficult and unsatisfactory as the rocks are more altered or metamorphosed. Various methods have been suggested to overcome the effects of alteration, especially oxidation, eg. Irvine and Baragar (1971). Norm calculations (reducing the Fe_2O_3 content to 1.5%) have been performed on metabasalts from the group. Most show an absence of normative hypersthene, with some hypersthene-normative, which is consistent with a variable alkali olivine basalt to tholeiite affinity. However, it should be noted that the altered state of these rocks does not permit unequivocal interpretation of magma type using CIPW norm calculations.

Pre-metamorphic petrographical features of the metabasaltic rocks (see section 2.6.4.2.) suggest they are spilites, ie. they have undergone secondary or autometasomatic alteration due to an interaction with seawater. This again inhibits the use of major element geochemistry and hence normative mineralogy in discriminating between alkaline and tholeiite magma types. The plot of Na_2O against CaO has been used to differentiate spilitized basalts from non-spilitized basalts (eg. Graham, 1976). Figure 2.6-18b shows that most of the metabasaltic pillow lavas and massive lava flows have anomalously high Na_2O abundances and fall within the spilite field. The high Na_2O and accompanying low CaO character of the metabasalts cannot be the result of igneous fractionation processes from a normal basaltic magma. In addition, the cores and rims of metabasaltic pillows, eg. specimens CC10 (66697) and CC7 (66698), and specimens CC4 (66696) and CC8 (66703), show compositional differences in CaO and Na_2O content, which probably result from increased spilitization at the margins of the pillows. Similar variations have been recorded from other pillow lavas (Vallance, 1965 and 1969; Graham, 1976).

Probably the most satisfactory method of defining the magma type of altered and metamorphosed basalts is through the use of immobile minor and trace elements (see Wilkinson, 1974; Floyd and Winchester, 1975 for discussion). The $TiO_2\%$ against Zr/P_2O_5 plot (Figure 2.6-18c) and the Nb/Y against Zr/P_2O_5 plot (Figure 2.6-18d), both after Floyd and Winchester (1975), are used in discriminating alkaline and tholeiitic suites. The Dunrossness spilite group metabasalts fall within the tholeiitic basalt field.

2.6.5.4 Basalt discrimination diagrams

The primary geochemical composition of volcanics is often masked by selective elemental mobility during spilitization and regional metamorphism. Concentrations of Ti, Zr and Y in basalts are considered to be relatively immobile during alteration and are frequently used in the characterization of magma type and the tectonomagmatic environment of eruption of ancient metabasic rocks (eg. Pearce and Cann, 1971, 1973; Floyd and Winchester, 1975; Winchester and Floyd, 1976). Cann (1970), Smith and Smith (1976) and Morrison (1978) have shown that there is no significant mobility of Ti, Zr and Y during low grade metamorphism of basalts. However, Hynes (1980) found that greenschist carbonate-rich metabasalts from the Quebec area, Canada, are depleted in Y and Zr and enriched in Ti; while low-carbonate samples are depleted in all three elements. In higher-grade amphibolite facies rocks Ti and Y are stable, and only a possible mobility of Zr is indicated (eg. Elliot, 1973; Field and Elliot, 1974; Winchester and Floyd, 1976).

In the metabasalts from the Dunrossness spilite group there is no mineralogical or geochemical evidence that Ti, Zr or Y have been affected by metamorphism. No concentrations of sphene or rutile are found in any of the samples. The metabasalts contain varying amounts of carbonate, but there is no systematic correlation between modal carbonate or wt% CaO and Ti, Zr or Y variation similar to that documented by Hynes (1980) for low-grade metabasalts. Therefore it is believed that Ti, Zr and Y may be used with confidence in distinguishing basalt tectonomagmatic environment(s) in this study.

Recent papers by Morrison (1978) and Holm (1982) have indicated that application and reliance on trace element discrimination diagrams alone can lead to erroneous conclusions on a basalts tectonic environment of eruption. Therefore, additional methods of geochemical discrimination have been applied. Along with the selected trace element discrimination diagrams in this section, rare earth element (REE) chondrite-normalized diagrams (see section 2.6.6.2) and multi-element N-type MORB-normalized diagrams (see section 2.6.5.4) are considered and discussed (see section 2.6.7). The basalt discrimination diagrams which best show the geochemical systematics of Dunrossness spilite group metabasalts and their tectonic environment of eruption are presented in Figure 2.6-19.

The Zr/Y v Zr diagram (Figure 2.6-19a) shows the pillow lavas and the majority of the massive lava flow metabasalts have affinities with modern, within-plate basalts (WPB). The Ti-Zr covariation diagram (Figure 2.6-19b) has two useful functions. First, the Ti/Zr ratio can be used to differentiate between intensely altered volcanic rocks of basic, intermediate or acid character (Winchester and Floyd, 1977; Stillman and Williams, 1977). The transition from basic to intermediate compositions is usually marked by the incoming of Fe-Ti oxide as a cumulus phase which causes a marked fall in the Ti/Zr ratio of the residual magma. A line dividing basic from more-evolved compositions has been drawn on the Ti v Zr diagram (Figure 2.6-19b). The diagram shows basic rocks are predominant within the group, but more-evolved rocks are also present (ie. the metadacite lava). The metabasalts and metadacite may also belong to the same fractionation trend in the diagram (cf. Alabaster et al., 1982). Second, the Ti v Zr diagram provides information on the eruptive setting of altered volcanic rocks (Pearce, 1980; Alabaster et al., 1982). The metabasalts are confirmed as being within-plate basalts (WPB), although a significant number of samples lie close to margin of the WPB field and within the MORB field. It may be that the Dunrossness spilite group metabasalts have a geoechemistry transitional between WPB and MORB.

The Dunrossness spilite group metabasalts and metadacite are plotted in a Cr v Y discrimination diagram in Figure 2.6-19c. The diagram uses the abundance of the immobile compatible element Cr as an index of fractionation, with the immobile incompatible element Y as the main geochemical discriminant. The diagram is of particular use in discriminating between IAT and MORB or WPB. Both metabasaltic pillowed and massive lavas plot within the WPB field and all but one metabasalt sample and the metadacite plot within the MORB field. The wide and near continuous variation in Cr abundance reflects significant differences in the crystal-liquid fractionation and/or partial melting histories of individual samples.

In the Nb v Zr v Y basalt discrimination diagram (Meschede, 1985; not shown here) Dunrossness spilite group metabasalts plot mostly within the within-plate tholeiite (WPT)/volcanic arc basalt (VAB) field. The Nb v Zr v Y diagram is specifically designed to discriminate between E (or P)-type MORB, N-type MORB and within-plate tholeiites (WPT), and therefore clearly precludes an E-type MORB or N-type MORB affinity for Dunrossness spilite group metabasalts.

2.6.5.5 Basalt multi-element diagrams

N-type MORB-normalized multi-element diagrams (spidergrams) have been widely used to highlight geochemical variations between basalts of different tectonomagmatic environments eg. Alabaster et al. (1982), Pearce (1983), Saunders and Tarney (1984) and Pearce et al. (1984).

Figure 2.6-20 is an N-type MORB-normalized multi-element diagram for massive metabasaltic and metadacitic lavas from the Dunrossness spilite group. The normalizing values and an explanation of the elemental ordering in the diagram is given in Appendix A1. The analytical data used in the diagram is given in Table 2.6-4.

The metadacite lava D14 (68143) shows an extreme depletion in the compatible elements Cr and Ni and is moderately depleted in Co; geochemical features to be expected for such an evolved magma. The incompatible high field strength (HFS) elements Ti, V and P also show extreme depletion relative to N-type MORB and may suggest that Fe-Ti oxide was a significant fractionating phase during the petrogenesis of the dacite magma. The P depletion is less easily explained, but may indicate that differentiation involved apatite fractional crystallization. Marked enrichment in other incompatible HFS elements (Hf, Zr, Nb), LREE (Ce, La) and large ion lithophile (LIL) elements (Th, Ba) is consistent with the highly-evolved nature of the dacite. However, the multi-element pattern as a whole does not prove amenable to qualitative tectonomagmatic interpretation and is plotted principally to show the compositional differences to the metabasalts of the Dunrossness spilite group.

Three massive metabasalt lava samples from the Dunrossness spilite group all have similar N-type MORB-normalized geochemical patterns (Figure 2.6-20). Compatible trace element (Ni, Cr, Co, Sc) abundances show a wide variation from about 0.3 to 2x N-type MORB probably reflecting variable degrees of fractionation of the metabasalt samples. All three metabasalt show lower Ni abundances relative to Cr. Incompatible HFS elements (V, Y, Ti, Sm, Hf, Zr, P Nd) form a near-flat trend subparallel to N-type MORB, but at a higher level. Incompatible LREE (Ce, La) and LIL elements (Ba, Rb, K) are similarly enriched relative to N-type MORB. However, the LIL element and LREE enrichment may be an artifact of secondary mobility and enrichment during regional metamorphism. The uniform enrichment of incompatible HFS elements, which are thought to be immobile during low- to medium-grade metamorphism, is similar to the multi-element patterns of E(enriched)-type MORB, within-plate continental and ocean island basalts, or more-evolved N-type MORB (cf. Alabaster et al., 1982; Pearce, 1983; Saunders and Tarney, 1984; Pearce et al., 1984).

Figure 2.6-21 shows N-type MORB normalized multi-element patterns for metabasaltic pillow lavas from the Dunrossness spilite group. Patterns for individual samples are very similar and are therefore discussed together. One feature that is immediately obvious from the patterns is that metabasaltic pillow lavas from Cunningsburgh and Levenwick have near identical multi-element curves, thus emphasising the correlation of the two main Dunrossness spilite group outcrops. Compatible trace element (Ni, Cr, Co) abundances in the metabasaltic pillow lavas are markedly enriched relative to the MORB normalizing value (1.5 to 3x N-type MORB) and suggest they are more primitive than the massive metabasaltic lavas; although the respective Mg′-values argue against this idea. The limited range of compatible trace element abundances is consistent with limited fractionation range within the metabasaltic pillow lava suite. Incompatible HFS elements are enriched relative to N-type MORB. Enrichment increases from R to L across the central portion of the diagram, so that V, Yb, Y and Ti show no enrichment relative to N-type MORB, whereas the more incompatible elements (Zr, P, Nb, Nd) show the greatest enrichment. Also, it is important to note that Nb is enriched to the level of adjacent elements (Ce, Nd, P) in the multi-element curves. LIL elements (Th, Ba, Rb, K, Sr) and LREE (Ce, La) are also enriched, generally with increased enrichment from L to R in the LIL element section. The result is a distinctive 'humped' multi-element pattern typical of basalts erupted in within-plate settings (continental or ocean island basalts) or along elevated mid-ocean ridge segments as E(enriched)-type MORB (cf. Alabaster et al., 1982; Pearce, 1983; Saunders and Tarney, 1984; Pearce et al., 1984).

2.6.6 REE geochemistry

2.6.6.1 Serpentinized ultramafites and steatites

REE analyses for serpentinized ultramafites from the Dunrossness spilite group are given in Table 2.6-5 and summarised graphically as a chondrite-normalized REE diagram in Figure 2.6-22.

The serpentinized peridotites BC230 (64779) and BC146 (62991) are characterised by low REE abundances (ca. 0.1 - 0.7 x chondrite) and distinctive shallowly concave-upwards REE profiles, with LREE to MREE enrichment (Ce_N/Sm_N = 1.89 and 1.51) and near flat MREE - HREE sections (Sm_N/Yb_N = 0.75 and 0.95). Assuming that they have not undergone significant secondary mobility and fractionation (an assumption which may be untenable given that the rocks are partially steatitized; see section 4.3), the serpentinized peridotites have REE profile characteristics similar, but not identical, to some Ophiolite complex mantle sequence harzburgites and dunites (see section 4.1).

Serpentinized pyroxenite BC41 (64113) has REE geochemical characteristics very different from the serpentinized peridotites of the Dunrossness spilite group. The serpentinized pyroxenite has REE abundances greater than chondrite (ca. 3 - 5.5 x chondrite), with a moderately LREE-enriched (Ce_N/Yb_N = 3.27), straight REE profile. The uniform LREE enrichment, high total REE abundances and straight profile shape are very similar to the REE profile characteristics of ultramafic cumulates from Layered complexes (see section 4.1). However, the serpentinized pyroxenite is heavily altered and any petrogenetic or tectonomagmatic interpretation must remain tentative give the possibility of REE mobility and fractionation with such alteration (see section 4.2 and 4.3).

REE analyses for steatites are presented in Table 2.6-6 and summarized in graphically as a chondrite-normalized REE diagram in Figure 2.6-22.

Steatite K2 clearly differs from the other steatites in REE geochemical characteristics despite having a similar modal mineralogy (see Appendix A6) and major trace element geochemistry (see section 2.6.5.1). The difference may reflect the fact that K2 is from near the Dunrossness phyllite group/Dunrossness spilite group boundary and/or because it contains modal chlorite. Steatite K2 shows a uniform LREE enrichment (Ce_N/Yb_N = 3.27), with REE abundances greater than chondrite and a straight REE profile shape, typical of ultramafites from Layered complexes (see section 4.1). REE profile characteristics for steatite K2 is similar in some ways to serpentinized pyroxenite BC41 and the steatite could represent a severe alteration product of this lithology, although the petrography and major and trace element geochemistry argue against this idea.

Steatites K32, K12 and K46 have REE profile characteristics broadly similar to the serpentinized peridotites BC230 (64779) and AC146 (62991), although with several individual REE anomalies. These steatites are probably derived from serpentinized peridotite protoliths, but have suffered selected REE mobility and fractionation during steatitization (see section 4.3 for discussion).

2.6.6.2 Metabasalts

REE analyses of metabasalts from the Dunrossness spilite group are presented in Table 2.6-5 and summarized graphically as a chondrite-normalized REE diagram in Figure 2.6-22.

The three metabasalts analysed all show moderate LREE enrichment relative to HREE (Ce_N/Yb_N = 2.30 to 3.85), with a constant normalized gradient from Lu to La and no meaningful Eu anomalies. All have high REE contents, between 8 and 60x chondrite. The pillow lava BC133 (64116) shows a slightly steeper REE profile (Ce_N/Yb_N = 3.85) than massive metabasalt BC241 (64148) and pillowed metabasalt BC123 (64114). The lower overall REE abundance of metabasalt BC241 (64148) compared with the two pillowed metabasalts suggest that BC241 (64148) has undergone a lower degree of fractionation; a conclusion supported by its markedly higher Mg′-value (see section 2.6.5.2).

Chondrite-normalized REE patterns have been used to interpret the eruptive setting and petrogenesis of basalts by a number of geochemists eg. Kay and Senechal (1976), Menzies et al. (1977) and Suen et al. (1979). However, the patterns are insufficient to uniquely identify the eruptive setting of the metabasalts. The Dunrossness spilite group metabasalts, with high REE abundance and moderate LREE enrichment, have patterns characteristic of within-plate, ocean island and continental basalts (Schilling and Winchester, 1966; McBirney and Williams, 1969; Schilling et al., 1976; Basaltic Volcanism Study Project, 1981; Saunders, 1984; Cullers and Graf, 1984) and some T (transitional)- and E(enriched)-type MORB (Schilling, 1975; Shibata et al., 1979; Sun et al., 1979; Basaltic Volcanism Study Project, 1981; Saunders, 1984). Recently, E-type basalts have been formed coexisting with N-type basalts in a normal mid-ocean ridge environment, such as those from DSDP Hole 504B of the Costa Rica Rift of the East Pacific Rise System (Tuel et al., 1985). Consequently an E-type MORB geochemistry does not rule out a 'normal' MOR environment of formation.

2.6.7 Summary and conclusion

(a) Contact relations between the Dunrossness spilite group and the statigraphically underlying Dunrossness phyllitic group are mostly affected by late, fault tectonism and the two groups appear tectonically interleaved in places. However, clear, gradational or transitionally interbedded, probable sedimentary contacts between metavolcaniclastic or black metasedimentary phyllite units of the Dunrossness spilite group and Dunrossness phyllitic group rocks are seen at several localities. These relations suggest these units of Dunrossness spilite group can be considered an integral part of the Dalradian-like portion of the East Mainland succession on Shetland.

(b) Gross stratigraphic considerations suggests the Dunrossness spilite group volcanism marked the culmination of a major basin-deepening sequence within the Dalradian-like portion of the East Mainland succession. The Scatsta division (L. Dalradian) and the Whiteness division (M. Dalradian) appear to be made up of shallow-water sediments and the upper portion of the overlying Cliff Hills division (M/U. Dalradian) comprise of turbiditic sediments with minor mafic volcanics and the Dunrossness spilite group. It is likely that the increasing tectonic instability recorded in the East Mainland succession was related to extension and faulting in the depositional basin.

(c) The Dunrossness spilite group is unconformably overlain by M. Devonian (Givetian) ORS sediments. This indicates that the group has undergone regional tectonometamorphism, uplift, exhumation and erosion prior to about 380 Ma (using the timescale of Harland et al., 1982).

(d) On lithostratigraphic grounds the Dunrossness spilite group may be a correlative of the lower units of the Southern Highland Group (U. Dalradian) of the Scottish Caledonides, which are characterised by widespread though sporadic volcanic sequences eg. Tayvallich Volcanics, Green Beds, etc. Faunal evidence within the Tayvallich Limestone, the upper-most unit of the Argyll Group (M. Dalradian) suggest a lower-most Cambrian age for the Argyll Group/Southern Highland Group boundary. Consequently, a lower Cambrian age is likely for the volcanic-bearing lower units of the Southern Highland Group and by inference the Dunrossness spilite group.

(e) An ^{40}Ar/^{39}Ar age spectrum for a whole-rock metabasalt sample from the Dunrossness spilite group gives a tentative igneous crystallization age of 587 ± 15 Ma. This data tends to confirm the lithostratigraphic correlation of the Dunrossness spilites with probable lower Cambrian (590 - 570 Ma, using timescale of Harland et al., 1982) volcanic sequences of the Southern Highland Group.

(f) Metabasaltic lava, metavolcaniclastite and metasedimentary units comprise a major part of the Dunrossness spilite group. The following lithologies occur within these units: massive metabasaltic lava flows, metabasaltic pillow lavas, plagioclase-phyric metabasalts, amygdaloidal metabasalts, metadacitic lavas, veins and tuffs, metavolcaniclastites, metavolcaniclastic phyllites, laharic (mud-flow) breccias, laminated graphitic quartzites (?recrystallized cherts), laminated black graphite-rich semipelitic and pelitic phyllites, laminated semipelitic and pelitic phyllites, quartz-plagioclase 'gritty' psammites, calc-silicate and dolomitic crystalline limestone layers.

Pillowed lava flows in the Dunrossness spilite group are prime evidence of a subaqueous environment of eruption. The facies association (including such lithologies as: calc-silicates, dolomitic crystalline limestones, laharic breccias, laminated black graphite-rich pelitic phyllites) and the underlying turbiditic sequence (Dunrossness phyllitic group) confirm a subaqueous, probable marine, volcanic/depositional environment.

The presence of amygdaloidal metabasaltic lavas in the volcanic sequence indicate that extrusion occur at relatively shallow-water depths. However, the water depth at which exsolution of magmatic volatiles can occur is variable and shows a crude correlation with magma composition, especially the original juvenile volatile content. In most basaltic magmas this depth is generally less than 1 km and for tholeiitic magmas is apparently less than 500 m (cf. Fisher, 1984; Kokelaar, 1986). Evidence of shallow-water eruption is also tentatively provided by the high proportion (up to 70% in some sections) of volcaniclastic material interbedded with the effusive lava flows in the Dunrossness spilite group. However, there is a possibility that the volcaniclastites are not the products of insitu explosive eruption caused by exsolution of magmatic volatiles. Many of the volcaniclastites may be the product of non-explosive fragmentation, which may occur at any depth, and others are clearly epiclastic deposits. The non-explosive volcaniclastic deposits include blocky, flow-top and inter-pillow breccias probably formed by cooling-contraction granulation. Epiclastic deposits include laharic (mud-flow) breccias, which are characteristically poorly sorted, poorly bedded, non-welded, matrix-supported, laminar mass flow deposits containing rip-up clasts. The laharic breccias probably developed from the slump and flow of water-saturated volcaniclastic debris on the subaqueous slopes of the volcanic edifice. Remobilization may have been the result of oversteepened volcanic debris or instability caused by contemporaneous seismic activity and/or eruption. The only clear evidence of pyroclastic activity (magmatic explosivity) in the volcanic sequence is the occurrence of rare, 'tear-drop' shaped lapilli in some laharic breccias. However, these lithic clasts may well be exotic (derived from outside the basin).

(g) Metabasaltic pillowed and massive lavas of the Dunrossness spilite group frequently display relic, possible spilitic, petrographic features, including, early, albite - epidote ± chlorite ± carbonate mineral assemblages. Also, a significant proportion of analysed metabasalts have anomalously high N_2O and accompanying low CaO abundances which cannot be readily explained under normal igneous fractionation processes. These metabasalts fall within the spilite field in the Na_2O v CaO diagram. Consequently, it is concluded from the petrographic and geochemical data that at least some of the metabasalts have undergone varying degrees of spilitization (autometasomatic interaction/ alteration with seawater).

(h) The altered and metamorphosed state of the metabasalts in the Dunrossness spilite group precludes an unequivocal interpretaion of the magma type using major element and normative compositions. However, the metabasalts all fall within the tholeiitic basalt field in the TiO_2 v Zr/P_2O_5 and Nb/Y v Zr/P_2O_5 diagrams which discriminate between alkaline and tholeiitic basalts on the basis of these selected immobile trace elements.

(i) The metabasaltic pillowed and massive lavas plot dominantly within the within-plate basalt (WPB) and MORB fields in the Cr v Y, Zr/Y v Zr and Ti v Zr basalt discrimination diagrams. In the Nb v Zr v Y diagram, which is specifically designed to discriminate between E (or P)-type MORB, N-type MORB and within-plate tholeiites (WPT), the *Dunrossness* spilite group metabasalts fall within the within-plate tholeiite (WPT)/volcanic arc basalt (VAB) field.

N-type MORB-normalized multi-element patterns for the massive metabasaltic lavas are similar to the multi-element patterns of E(enriched)-type MORB, more-evolved N-type MORB, and within-plate continental and ocean island basalts. N-type MORB-normalized multi-element diagram for the metabasaltic pillow lavas show the distinctive 'humped' multi-element patterns typical of basalts erupted in within-plate settings (continental or ocean island basalts) or along elevated mid-ocean rige segments as E(enriched)-type MORB.

The Dunrossness spilite group metabasalts, with high REE abundances and moderate, uniform LREE enrichment, have REE profile characteristics typical of within-plate basalts and E(enriched)-type MORB.

Taken together the basalt discrimination diagrams, N-type MORB-normalized multi-element diagrams and REE profile characteristics suggest a within-plate tholeiite affinity for the metabasalts from the Dunrossness spilite group.

(j) The massive metabasaltic lava compositions form a continuous trend on $100Mg/(Mg + Fe^{2+})$ variation diagrams and are consistent with differentiation controlled by mafic mineral (probably olivine and pyroxene) fractional cyrstallization. Compatible and incompatible trace element trends in the $100Mg/(Mg + Fe^{2+})$ variation diagrams effectively preclude the massive metabasaltic lavas and metabasaltic pillow lavas being petrogenetically related by high-level fractional crystallization processes. Similarly, N-type MORB-normalized multi-element diagrams highlight a number of distinct geochemical differences between the massive metabasaltic lavas and the metabasaltic pillow lavas. The distinctly different multi-element patterns for the two rock suites suggest they cannot be related by high-level fractional crystallization.

(k) Serpentinized ultramafites form a significant part of the Dunrossness spilite group, with massive and spinifex-like textured serpentinized peridotites preserved in one structural unit in the Cunningsburgh area. The massive serpentinized peridotites have a cumulate appearance. The spinifex-like textured serpentinized peridotites comprise early, elongate, olivine pseudomorphs, either randomly arranged, or as closely, packed subparallel arrays with perpendicular or imbricate alignment to textural/grain size layering.

The spinifex-like textured serpentinized peridotites petrographically resemble spinifex textured peridotitic komatiites, some jack-straw textured (pseudo-spinifex, elongate, metamorphic, porphyroblastic, olivine growth ultramafites), and some crescumulate ultramafites from layered complexes (cf. Donaldson, 1974, 1982; Lofgren and Donaldson, 1975; Irvine, 1982). The volcanic and plutonic varieties are the product of rapid crystallization induced by olivine supersaturation and/or supercooling of the *parent melt*. *Volcanic*, metamorphic and plutonic examples are remarkably similar and criteria for distinguishing between the similar textures are not well established for all cases. *However*, *examples* of jack-straw texture can differ significantly from the igneous textures. The metamorphic olivines are not skeletal, are unusual in being elongate parallel to [010] rather than the more common [100] and [001] directions, can be seen to cross cut earlier foliations and tend to have a cigar-shaped outline (possibly related to the unusual elongation direction). Cross-cutting elongate olivine grains are found in both the igneous and metamorphic textures, but metamorphic elongate olivines are thought not to form euhedral crystal terminations at the point where two elongate olivines appear to cross; a feature common in spinifex textured peridotitic komatiites. (R.W. Nesbitt, pers. comm.). The reason for the latter distinction is unclear, but it is accepted that elongate growth in solid state and magmatic states may represent fundamentally different processes. Nevertheless, it is still hard to envisage how growth in a particular orientation/direction across an intervening crystal, in either a metamorphic or magmatic system, could be maintained if the elongate crystal did actually terminate. It is more likely that the two portions of a cross-cutting crystal only appear to terminate within the plane of the section, but are in fact linked.

Elongate olivines within Dunrossness spilite group spinifex-like textured serpentinized peridotites show textural similarities with both igneous and metamorphic elongate olivines. The spinifex-like textured serpentinized peridotite elongate olivines do not appear skeletal or embayed (although the pseudomorphic textures are rather crude and fine details may have been overprinted), but are tabular and parallel sided, do not cross cut earlier foliations, and show both euhedral crystal terminations and non-terminated cross-cutting olivine relations. Additional textural differences exist between the spinifex-like textured serpentinized peridotites and spinifex textured peridotitic komatiites and these include a lack of obvious intersertal glass or interstitial delicate clinopyroxene growths. Inter-olivine areas in the spinifex-like textured serpentinized peridotites are composed of non-pseudomorphic, granular carbonate ± talc ± magnetite.

Other early petrographic features of the Dunrossness spilite group serpentinized peridotites are also not helpful in distinguishing between origins for the ultramafites. Randomly orientated, elongate olivine textures in the serpentinized peridotites show overall textural similarities with some random spinifex (upper A_2 zone) peridotitic komatiites (cf. Donaldson, 1982, Figure 16.6a) and the closely packed, subparallel arrays of perpendicular or imbricate aligned elongate olivine textures resemble some plate spinifex (lower A_2 zone) peridotitic komatiites (cf. Donaldson, 1982; Arndt, 1985). Massive ?cumulate serpentinized peridotites from the Dunrossness spilite group resemble cumulate (B zone) peridotitic komatiites (cf. Donaldson, 1982; Arndt, 1985), and as in peridotitic komatiites the spinifex-like rocks are poorer in olivine than the massive cumulate rocks. However, similar randomly orientated and plate elongate olivine textures are recorded from crescumulate units of layered intrusions (Donaldson, 1974 and 1982; Lofgren and Donaldson, 1975). Donaldson and co-workers have shown that the size of the crystals and the skeletal and dendritic shapes characteristic of rapid growth cannot be used to differentiate between volcanic and plutonic crystallization environments. Supersaturation in both environments produces close similarities in the shapes and sizes of olivine in both plutonic crescumulate and volcanic spinifex rocks.

(1) Massive and spinifex-like textured serpentinized peridotites are disrupted at numerous localities and occur as blocky, matrix-poor brecciated units. Owing to poor exposure and incomplete sections within the massive and spinifex-textured serpentinized peridotites and brecciated varieties of these rocks it is not possible to define clearly the relationships between the lithologies. It is possible the brecciation is an autoclastic phenomena developed during extrusion or intrusion and final solidification of the ultramafite masses. Similar brecciation is a common feature of peridotitic komatiites and may affect the whole or a major part of a particular flow (cf.

Arndt et al., 1977; Donaldson, 1982; Aitken and Echeverria, 1984). Alternatively, the brecciation may represent quasi, semi-ductile deformation synchronous with serpentinization (cf. Coleman, 1971 and 1977).

(m) Throughout the Dunrossness spilite group the serpentinized ultramafites appear to be interbedded or interleaved with metabasaltic lavas and metavolcaniclastic units. Unfortunately, contacts of the ultramafites are heavily steatitized and sheared, therefore, pre-tectonic relations are not discernable.

(n) Coarse, cumulate-like textured serpentinized pyroxenite in the Dunrossness spilite group shows REE profile characteristics very different to the serpentinized peridotites (see section 2.6.6.1) which suggest the two ultramafic rock types are not directly petrogenetically related. Ultramafite REE discrimination techniques identify the serpentinized pyroxenite as a probable Layered complex ultramafite (see section 4.4 and 5.2.1).

(o) Massive and spinifex-like textured serpentinized peridotites from the Dunrossness spilite group have similar major, trace and rare earth element abundances. The serpentinized peridotites as a whole have highly magnesian bulk compositions, with high compatible trace element abundances and very low incompatible trace element abundances. Steatites mostly have major and trace element characteristics similar to the serpentinized peridotites, but with a greater variability in some elements. The variability in these elements may be the result of selected elemental mobility and fractionation during steatitization.

Whole-rock major and trace element geochemical comparison between the Dunrossness spilite group serpentinized peridotites and published analyses of peridotitic komatiites show the latter are significantly richer in CaO, Al_2O_3, Na_2O and most incompatible trace elements (cf. BVSP, 1981; Jahn et al., 1982; Berswick, 1982, 1983; Barnes et al., 1983; S-Seymour et al., 1983; Arndt, 1985; Arndt and Jenner, 1986). The serpentinized peridotites have higher Mg′-values and dominantly higher MgO, Ni and Cr values than peridotitic komatiites (both cumulate and spinifex varieties). If the geochemistry of the spinifex-like textured serpentinized peridotite, or indeed any of the serpentinized peridotites, is accepted as close to melt composition (although there are problems with this assumption, even in Archean peridotitic komatiites, cf. Berswick, 1983; Arndt, 1986) then prohibitively large degrees of partial melting of a very refractory mantle source would probably be required (cf. Arndt, 1977; BVSP, 1981; Bickle, 1982). However, recently Takahaski and Scarfe (1985) have shown in very high pressure experimental studies that peridotitic komatiite magmas could be produced by small degrees of mantle partial melting at depths of 150 - 200 km. Nevertheless, even at these very high pressures, where there is a close approach of the mantle solidus and liquidus, a refractory (?harzburgite) source would be required. It is unlikely that such a source would be available at depth, given the relatively low density of mantle harzburgite.

An additional problem is posed by the fact that any proposed very high magnesian melt would have a high eruption temperature and low viscosity (cf. Bickle, 1982; Arndt and

Nisbet, 1982) and would be expected to flow turbulently during travel to the surface and eruption (Huppert et al., 1984). These characteristics mean the melt would tend to thermally erode and become contaminated by the rocks it intrudes or is erupted onto. Consequently, the melt would probably be expected to become less magnesian and richer in lithophile elements. Clearly, there is no scope for any such contamination of a melt of the composition of the spinifex-like textured serpentinized peridotite from the Dunrossness spilite group.

Given the considerable geochemical differences between the Dunrossness spilite group *serpentinized peridotites* and peridotitic komatiites and the difficulties *in generating* and preserving a melt of the spinifex-like textured serpentinized peridotite composition, it seems probable that the serpentinized peridotites are not of peridotitic komatiite composition.

(p) Ultramafite REE discrimination techniques applied to both the serpentinized peridotites and steatites fails to define a likely tectonomagmatic affinity for most of the rocks (see section 4.4 and 5.2.1). Steatite K12 is identified as an Ophiolite complex mantle sequence harzburgite or dunite and the other serpentinized peridotites and steatites show similar REE profile characteristics to this sample. However, the REE discrimination results should be treated as suspect and interpreted with caution given the possibility that the altered ultramafites may have undergone secondary REE mobility and fractionation (see section 4.2, 4.3 and 5.2).

(q) Given the ambiguities in field and petrographical features and the real difficulties in interpreting the whole-rcok geochemistry of the serpentinized peridotites from the Dunrossness spilite group, it is felt that the data does not provide any clear, consistent indication of the tectonomagmatic affinity of these ultramafites. Nevertheless, major, trace and REE abundances are broadly similar to many Ophiolite complex mantle sequence harzburgites (eg. see section 2.10) and substantial differences in geochemical characteristics compared to Peridotitic komatiites exist. If the field and petrographic data are accepted to indicate a Peridotitic komatiite affinity then it would probably be necessary to argue that wholesale secondary metasomatic alteration in the serpentinized peridotites had occurred.

(r) Metamorphic assemblages in Dunrossness spilite group rocks (see section 2.6.4) are variable, but generally reflect a main, syn-kinematic, lower-middle amphibolite facies episode. Garnet - biotite geothermometry give a temperature estimate of the late-stage metamorphic conditions of about 497 °C.

^{40}Ar/^{39}Ar spectra for two whole-rock metabasalts from the Dunrossness spilite group both give well-defined, major plateaux with apparent ages of 490 ± 6 Ma and 486 ± 7 Ma. This ca. 490 Ma event is interpreted to represent ^{40}Ar/^{39}Ar system closure in hornblende, the prinicipal K-bearing (and probable Ar-bearing) mineral phase within the rocks, at or near the time of the peak of regional metamophism. This metamorphic event is clearly Caledonian in age and corresponds exactly with the time of the Grampian D3 regional metamorphic peak within the Scottish Caledonides which is known to be about 515 - 490 Ma.

(s) Field and $^{40}Ar/^{39}Ar$ radiometric data suggest that a proportion of the numerous, isolated, minor hornblende gabbro and diorite masses which lie within the Dunrossness spilite group outcrop are essentially post-tectonic and intruded at 461 ± 3 Ma.

2.7 Ultramafites within the Scatsta division on Unst

The Unst zoned ultramafic bodies are a series of concentrically zoned ultramafic bodies that occur within the Dalradian-like Scatsta division on the W side of Unst (Figure 2.7-1). The bodies all lie within the Valla-Field block (sensu Read, 1934). The metamorphic rocks of this tectonic unit are mostly metasedimentary or metaigneous schists and gneisses. Read (1934 and 1937) stated that the block was affected by three metamorphic episodes. The first is a main syn-deformational regional episode which reached kyanite grade amphibolite facies conditions of metamorphism. Pelitic rocks develop a kyanite-staurolite-garnet-biotite-muscovite assemblage and calc-silicate lithologies show a diopside-biotite-epidote-idocrase-plagioclase parageneic assemblage from this metamorphic episode. The episode is accompanied by widespread migmatisation and veining by granitic pegmatites. The second, retrograde episode affects the southern part of the block. Kyanite and staurolite are variably replaced by chloritoid and chlorite in pelitic lithologies. In the calcareous rocks diopside is converted to tremolitic amphibole. The third metamorphic episode ('dislocation metamorphism') is confined to a zone adjacent to the thrust margin of Shetland ophiolite and is characterised by the development of chloritic shear zones trending approximately N-S.

Flinn (1958), in a reappraisal of Read's work, recognised kyanite remained stable into the second episode, giving the paragenic assemblage kyanite-chlorite-chloritoid. It was also recognised that rocks within the ophiolitic melange, the Muness phyllite group, showed evidence of the effects of two metamorphic episodes. The first of these episodes Flinn chose to correlate with Read's second metamorphic episode of the Valla Field block.

More recent work by Aziz (1984) has reassessed and partially modified the metamorphic history of the Valla Field block, but again Read's original 'three metamorphisms' remains essentially intact.

The Valla Field block is bounded to the E by the thrust-melange system at the base of the Shetland ophiolite and to the W by the Bluemull Sound fault (Figure 1.2-2). Schist within the block strike approximately N-S and for the most lie on E limb of a major antiformal structure whose axial trace lies on or around the Bluemull Sound. Evidence from small scale structures indicate the rock of the Valla Field block have undergone polyphase deformation both accompanying and post-dating the main metamorphic episode.

The Scatsta division is correlated, on lithostratigraphical grounds, with the lower Dalradian Appin Group of the Scottish Caledonides (Flinn et al., 1972, 1979; Harris and Pitcher, 1975). K-Ar radiometric dating give a range of ages between 396 ± 10my and 515 ± 5my (Miller and Flinn, 1966). These ages are thought to represent K-Ar closure after the peak of regional metamorphism and are broadly comparible with those for the rest of the Dalradian Supergroup (Brown et al., 1965; Dewey et al., 1970; Dempster, 1985)

2.7.2 Details of exposures

Figure 2.7-1 shows the locations of ultramafic bodies within the Valla Field block on Unst. All are on the coast with the exception of Clammel Knowes [HP 5836 0639], a large body (15 x 10 m), elongate WNW-ESE which has been quarried out. The bodies occur at all structural levels within the Valla Field block on Unst and are associated with a variety of rock types, including quartzo-feldspathic gneisses, amphibolites and garnet-amphibolite gneisses, and pelitic gneisses (Read, 1937; Flinn, 1958). The bodies range in diameter from ca. 10 cm (Figure 2.7-2d) up to ca. 15 m. They are enclosed within the metasedimentary and metaigneous gneissose schists and wrapped by the main penetrative tectonic foliation (Figure 2.7-2 a and d). This foliation is in places blastomylonitic. Most bodies are podiform (Figure 2.7-2b) or near spherical (Figure 2.7-2a and c) in shape. At Lunda Wick [HP 5662 0443] three large (2.5-4 m diameter) and several smaller ultramafic bodies lie approximately along strike from each other. The bodies may have been one continuous unit, since disrupted in the main foliation-producing deformation episode. The ultramafic bodies are all mineralogically zoned (Figure 2.7-2c and d). The zonal structure of the individual bodies is detailed in Read (1934). Read (1934) and later Curtis and Brown (1969, 1971) described the idealised zonal arrangement. The ideal zonal sequence is most completely developed in the larger ultramafic bodies, eg. Lunda Wick (Figure 2.7-2a, b and c), which consists of successively developed antigorite, talc, tremolite-actinolite, chlorite and phlogopite zones. The idealised zonal arrangement comprises the following mineral assemblages (not necessarily equilibrium assemblages): antigorite zones = antigorite + brucite + magnesite ± talc ± chlorite; talc zone = talc + magnesite; tremolite-actinolite zone = tremolite-actinolite + talc ± magnesite ± chlorite; chlorite zone = chlorite ± tremolite-actinolite ± talc; phlogopite zone = phlogopite ± chlorite (phlogopite breaks down to a sodium vermiculite (Curtis et al., 1969).

The tremolite-actinolite zones can frequently be subdivided into layers of differing grain-size and grain orientation, with either radial or non-oriented elongate prisms. The tremolite, chlorite and phlogopite zones have a total width usually less than ca. 15 cm (Figure 2.7-2 c and d). Boundaries between all the zones are sharp (<1 cm wide) with definition of the boundaries generally increasing from the antigorite-talc junction to the chlorite-phlogopite junction.

The ultramafic bodies are in general similar to other concentrically zoned ultramafic bodies described by Phillips and Hess (1936), Chidester (1962, 1967), Matthews (1967), Cooper (1976), Brady (1977), Fowler et al., (1981) and Koons (1981).

2.7.3 Petrography and geochemistry

The antigoritite from the central core of the zoned ultramafic bodies show a non-pseudomorphic interpenetrative bladed-mat type γ-serpentine texture with poor preferred alignment of γ-serpentine parallel with foliation in the 'country rock' gneissose schists. The serpentinite lacks any obvious γ-serpentine bastites which tends to suggest the protolith was an olivine-rich peridotite or dunite. Magnesite, talc, magnetite and chlorite occur as intergranular accessory phases within the central core regions. The stability fields of the central core minerals indicate tht the temperature of formation was below about 500 °C; γ-serpentine becomes unstable and is replaced by a forsterite + talc + H_2O pargenic assemblages above 500 °C. Within the talc zones magnesite and talc occur in approximately equal proportion and have a homogeneous, fine-grained granular texture. Tremolite-actinolite of the actinolite zones occurs as interpenetrating non-oriented or radially oriented euhedral prism with minor accessory intergranular talc, magnesite and chlorite. The chlorite zones are near monomineralic non-oriented chlorite. Similarly, the phlogopite zones are near monomineralic phlogopite with accessory chlorite, mineral phases are invariably oriented parallel (tangential) to the margin of the ultramafic body.

Read (1934) stated that the ultramafic bodies developed their zonal structure during a metasomatic episode coincident with the first amphibolite-facies metamorphism. However, the lack of preferred mineral alignment in the majority of the outer zones suggests that mineral growth post-dated, or at least continued beyond the main deformation-metamorphic event.

Major and trace element data for whole rock samples from two major zoned ultramafic bodies at Lunda Wick [HP 5562 0443] and Clay Geo [HP 5745 0767] are given in Table 2.2-1 and in Curtis and Brown (1969, 1971). Elemental distribution within the mineralogical zones for the two bodies is summarized graphically in Figure 2.7-3. The major and trace element variation is similar to that reported by Matthews (1967), Koons (1981) and Fowler et al., (1981). The MgO profile shows a steady continuous decrease into the 'country rock' schists. The SiO_2 profile is relatively uniform with an increase into the talc and actinolite zones and a decrease into the chlorite and phlogopite zones. There is a marked discontinuity in relative Al_2O_3 content between the actinolite and chlorite zones. CaO shows a sharp decrease through the antigorite and talc zones, with a peak in the actinolite zones. The K_2O profile peaks from the 'country rock' schists into the phlogopite zone, with variably low abundances in other zones. Trace elements Cr, Ni and Mn behaved, for the most, coherently with MgO during metasomatism, although Cr does show strong relative depleation in the chlorite and phlogopite zones. Ba, as with the K_2O profile, increases in abundance from the 'country rock' into the phlogopite zone. Sr behaved coherently with Na_2O and decreases markedly out of the 'country rock' schists into the ultramafite. The observed geochemical coherence of these trace and major elements can be explained by consideration of their similar charges, ionic radii, or by crystal-fields effects.

Curtis and Brown (1969, 1971) placed the ultramafite-'country rock' boundary at the outer margin of the phlogopite zone. However, the geochemical profiles show no obvious static marker element(s) which would identify this original boundary. Brady (1977) and Koons (1981), working on similar zoned ultramafic bodies from Skye and Pounamu, New Zealand respectively, placed the ultramafite - 'country rock' boundary between the tremolite and chlorite zones on the basis of a marked perturbation in the Al_2O_3 profile. They considered Al_2O_3 was immobile during metasomatism. The Unst zoned ultramafites show a similar marked Al_2O_3 discontinuity at the tremolite-chlorite boundary. However, Al_2O_3 abundances in the chlorite zone are slightly higher than in the country rock schists which may indicate a degree of Al mobility. Similar Al_2O_3 enrichment in the outermost metasomatic zones is reported from zoned ultramafic bodies in Fiskenasset, Greenland (Fowler et al., 1981). It is therefore clear that an unequivocal identification of the original contact is not possible. Consequently, any quantitative analysis of elemental diffusion in and out of the ultramafic using mass balance calculations is severely hampered.

The form of profiles in Figure 2.7-3 highlights a series of elemental culminations in specific zones, with Ca in actinolite, Al in chlorite, Si in talc and actinolite, K in phlogopite. These features are typical of metasomatic reaction zones involving diffusive transfer along chemical potential gradients where local equilibrium is established in that gradient (Thompson, 1959; Korzhinskii, 1970). On this basis the mineralogical zonation and associated elemental distributions can be explained in terms of a relatively simple diffusion model, with variable mobility (effective transport velocity) of volatile and non-volatile components between the two rock types.

The spherical arrangement of mineral zones is consistent with diffusion metasomatism in a pervasive intergranular fluid phase medium (Hofmann, 1972). Curtis and Brown (1969) suggested that the fluid phase was supercritical in nature. The hydrous nature of minerals within all zones of the ultramafic bodies points to metasomatism involving H_2O and H+. CO_2 migration from the 'country rock' schists into the ultramafite, as evidenced by the occurrence of magnesite in the talc zones and to a lesser degree in the antigorite zones, is also apparent. Superimposed on this volatile metasomatism is a sequence controlled by diffusion on non-volatile components. Introduction of SiO_2 into the ultramafite resulted in the development of the talc zones. Formation of the tremolite zone involved transfer of CaO into the ultramafite *concomittant* with the outward diffusion of MgO into the 'country rock'. Formation of the chlorite probably involved a rise in MgO and Al_2O_3 into a presumed 'country rock' schist reaction zone. Marginal enrichment in K_2O from the 'country rock' into the schist reaction zone gave rise to the phlogopite zones. The inferred relative rates of elemental diffusion controlling the formation of reaction zone assemblages are consistent with the finding of Idlefonse and Gabis (1975) which show that CaO and MgO diffuses slowly compared to SiO_2. Under this model it is assumed that the antigorite zone at the core of many of the larger ultramfic bodies in W Unst has suffered only 'simple' hydration and carbonization. If this assumption is valid the composition of the antigorite serpentinite (Table 2.2-1) is consistent with a dunite or olivine-rich peridotite protolith.

2.7.4 Summary and conclusions

Field, petrological and geochemical features of the ultramafites suggests the following geological history.

(a) Intrusion or inclusion of the minor dunitic or peridotitic bodies in association with basic magmatic, pelitic, semipelitic, psammitic and calcareous rocks.

(b) Partial disruption of the ultramafic bodies in the main tectonometamorphic episode(s), possibly accompanied by initial serpentinization.

(c) Development of the metasomatic zonation penecontemporaneous and outlasting the main tectonometamorphic episode(s), with final equilibrium below about 500 °C. Metasomatism involved elemental transfer between ultramafite and 'country rock' gneisses, probably in a supercritical fluid phase medium. Individual mineralogical zones show specific elemental culminations typical of diffusive transfer along chemical potential gradients where local equilibrium is established in the gradient.

2.8 Ultramafites within the Scatsta division on Whalsay and Lunning

2.8.1 Geological setting

The Scatsta division of the East Mainland succession (Flinn et al., 1972) crops out over much of the NE part of the Shetland mainland E of the Nesting Fault and on Whalsay (Figure 1.2-2). The division is regarded as a probable correlative of the Appin Group (L. Dalradian) of the Scottish Caledonides (Flinn et al., 1972, 1979; Harris and Pitcher, 1975). Ultramafites within the Scatsta division occur in coarse micaceous schists and gneisses (Scatsta pelitic group) and in interbanded quartzites and pelitic to semipelitic schists. The ultramafites are numerous and are exposed in three main areas (Figure 1.2-2): (a) on the northern half of the island of Whalsay, GR: [HU 55 63]; (b) in the Lunning area, GR: [HU 50 65], and (c) at The Taing, NW of Lunning, GR: [HU 492 678].

2.8.2 Details of exposure and rock types

2.8.2.1 Whalsay ultramafites

Six, separate, minor, serpentinized ultramafite masses crop out in northern Whalsay. Four of the ultramafites are not exposed, or no exposure has been found, and are defined by magnetometer survey, these include: (a) Henri Geo ultramafite (GR: [HU 5715 6676]); (b) Bratti Geo ultramafite (GR: [HU 5658 6560]); (c) Brough ultramafite (GR: [HU 5580 6505]), and (d) an unnamed ultramafite at GR: [HU 5410 6360]. Another ultramafite body, the Newpark ultramafite is exposed at GR: [HU 5491 6472] and is a ca. 5 m long, concordant, podiform, serpentinized pyroxene-rich peridotite mass. A larger body, the Marrister ultramafite, is exposed at GR: [HU 5428 6381] and forms an isolated, 10 x 25 m, NE-SW trending knoll of serpentinized peridotite.

2.8.2.2 Lunning ultramafites

Numerous, minor(< 20 m across), podiform, ultramafite masses (Figure 2.8-1a) are exposed in the Lunning area and the lithologies include: (a) serpentinized dunite at GR: [HU 4532 6735] and GR: [HU 4556 6695]; (b) coarse serpentinized pyroxenite (Figure 2.8-1c) at GR: [HU 4537 6636] and GR: [HU 4556 6669], and (c) phase or modally layered serpentinized peridotite (Figure 2.8-1b) at GR: [HU 4528 6708], GR: [HU 4532 6708], GR: [HU 4535 6711], GR: [HU 4526 3712], GR: [HU 4518 6659] and GR: [HU 4534 6717]. A major ultramafite mass forms a complex discordant outcrop N of Lunning (cf. BGS sheet, 128, 1981) at GR: [HU 457 671] and is exposed both inland and on the coast at Orr Wick (GR: [HU 4558 6733]). In the coastal exposures phacoidal antigorite-serpentinite masses are partially steatitized and in places show a well-developed mineralogical zonation very similar to some ultramafites elsewhere in Shetland (eg. see section 2.7). Inland exposures consist of variously serpentinized dunite, harzburgite or lherzolite, with relic, probable igneous minerals preserved in places. Most of the ultramafite lithologies are homogeneous (Figure 2.8-1d), but occassionally phase and modal layering is seen (eg. GR: [HU 5074 6717]). Contacts between the ultramafite and 'country-rock' schist are locally discordant and appear intrusive (eg. GR: [HU 5077 6720]).

2.8.2.3 The Taing ultramafite

A small, 3 m wide, E-W trending, concordant, podiform, altered-ultramafite body is exposed ca. 50 m S of The Taing at GR: [HU 492 678]. The ultramafite is concentrically zoned with the core of coarse, acicular tremolite and actinolite probably after pyroxene.

2.8.3 Summary and conclusions

(a) Ultramafites within the Scatsta division on Lunning and Whalsay are, on the whole, less deformed and altered compared to those within the Scatsta division on Unst (see section 2.7).

(b) Probable igneous mineralogical and petrographical features, including phase and modal layering, are well preserved in some of the ultramafites.

(c) The ultramafites consist of variably serpentinized and/or amphibolited dunites, peridotites (harzburgite and lherzolites) and pyroxenites.

(d) The margins of the ultramafites are mostly concordant and are wrapped by the regional metamorphic foliation. However, in the main Lunning ultramafite discordant intrusive-like contacts are seen and suggest the body is a syn- to late-tectonic intrusive mass.

2.9 Ultramafites within the Queyfirth unit

2.9.1 Geological setting

The Queyfirth unit, formerly the Queyfirth group (Pringle, 1970; Robinson, 1983), crops out as an elongate tract running down the NE side of the northern Shetland mainland and forms the southern tip of Hillswick Ness (Figure 1.2-2 and 2.2-1). The tectonostratigraphic unit lies W of the Walls Boundary fault and is separated from the underlying Sand Voe unit (see section 2.2) by a major tectonic discontinuity - the Virdibreck shear zone (Figure 2.2-1). The succession within the unit is difficult to establish because of frequent faulting and complex, tight to isoclinal, westward-verging, Caledonian folding. Rocks within the Queyfirth unit include: heterogeneous greenschists (U. Dalradian-like 'greenstones'), metagabbros, serpentinized ultramafites, graphitic phyllites, impure quartzites, calcareous semipelites, siliceous limestones, pelitic schists, schistose conglomerates, and interbanded semipelites and impure flaggy quartzites. The rocks have been correlated on a lithostratigraphic basis with the Southern Highland Group (U. Dalradian) of the Grampian Highlands of Scotland (Flinn et al., 1972; 1979; Robinson, 1983).

Metaigneous rocks within the Queyfirth unit include: metagabbros and serpentinized ultramafites. These lithologies generally occur as concordant masses within greenschist of the Queyfirth unit (Figure 2.2-1) and contacts with surrounding metasediments are sheared. The most important of the metagabbroic masses within the unit is the Skinisfield metagabbro which crops out on the Fethaland peninsula. $^{40}Ar/^{39}Ar$ dating of hornblende from the metagabbro gives a well-defined plateau age of 439 Ma (Robinson, 1983) and probably indicates a post- to late-tectonic igneous crystallization age for the mass. Serpentinized ultramafites within the Queyfirth unit are numerous and are exposed in eight separate areas

(Figure 2.2-1): (a) Gro Stack and Tuska Skerry, Hillswick Ness, GR: [HU 265 748]; (b) Burgan, near N Gluss, GR: [HU 345 779]; (c) Roonan, near N Gluss, GR: [HU 342 782]; (d) Burn of Leean, S of Quey Firth, GR: [HU 353 813]; (e) Ness of Queyfirth, GR: [HU 357 826]; (f) Head of Calsta, S of Burra Voe, GR: [HU 376 878]; (g) Cleber Geos, Fethaland, GR: [HU 378 946]; (h) Point of Fethaland, GR: [HU 379 949].

2.9.2 Details of exposure and rock types

2.9.2.1. Gro Stack and Tuska Skerry ultramafites

(a) A 12 x 16 m, concordant, antigorite-serpentinite sliver cut by numerous anastomosing steatitized shear zones is exposed in pelitic schists at the cliff top opposite Gro Stack at GR: [HU 2757 7490].

(b) A 12 m wide, tabular, concordant antigorite-serpentinite body is exposed in a steep, fault-zone gully below the Hillswick Ness lighthouse at GR: [HU 2781 7455].

2.9.2.2 Burgan ultramafite

A ca. 450 m long, 50 - 70 m wide, tabular, NNE-SSW trending, concordant, massive, serpentinized dunite mass is exposed NW of N Gluss at GR: [HU 3438 7765].

2.9.2.3 Roonan ultramafites

(a) A large, poorly exposed, irregular shaped, serpentinized dunite and pyroxenite mass (defined mostly by a > 1000 gamma positive magnetic anomaly) is exposed NE of the Roonans at GR: [HU 3420 7815].

(b) A small, 10 x 30 m, tabular, serpentinized ultramafite mass crops out S of the junction of the B9079 and A970 at GR: [HU

3372 7860] and is defined by a concentration of ultramafite boulders and a > 1000 gamma positive magnetic anomaly.

2.9.2.4 Burn of Leean ultramafite

A major, ca. 1.3 km long, NNE-SSW trending ultramafite body lying approximately along the Virdibreck Shear is exposed at GR: [HU 3535 8115]. The ultramafite consists of serpentinized dunite with occassional chromite dunite layering (eg. GR: [HU 3540 8136]. A (?) separate layered, serpentinized pyroxenite-dunite body crops out E of Burn of Leean at GR: [HU 3540 8112]. Both bodies are defined by well-developed positive magnetic anomaly systems.

2.9.2.5 Grunans and Nes of Queyfirth ultramafites

(a) Four, minor, poorly exposed, serpentinized ultramafite slivers crop out S of Grunans at GR: [HU 3570 8226].

(b) A ca. 40 x 150 m, NNE-SSW trending, (?)serpentinized ultramafite body is defined by a > 1000 gamma positive magnetic anomaly at GR: [HU 3610 8256].

2.9.2.6 Head of Calsta ultramafites

Two complexly sheared and mineralogically, zoned steatite/antigorite-serpentinite masses are exposed in the cliff section at GR: [HU 3765 8774] and GR: [HU 3756 8780] (cf. Pringle, 1970, Figure 9).

2.9.2.7 Gleber Geos ultramafites

(a) A 20 m wide, tabular, steatite/antigorite-serpentinite body is exposed at GR: [HU 3775 9432].

(b) A ca. 60 m wide, (?)circular ultramafite crops out at GR: [HU 3780 9448] and comprises numerous antigorite-serpentinite phacoids separated by steatitized shear zones.

2.9.2.8 Point of Fethaland ultramafite

A minor (< 5 m wide), steatitized ultramafite mass is exposed at GR: [HU 3795 9497]. The ultramafite is sheared and occupies a late-fault zone and cross cut the foliation in the surrounding pelitic schists.

2.9.3 Summary and conclusions

(a) Ultramafites within the Queyfirth unit are often variably altered to steatite and antigorite-serpentinite lithologies, but are clearly recognisable as serpentinized dunites and pyroxenites in some ultramafite bodies.

(b) The ultramafites are mostly concordant and everywhere have sheared or faulted margins with surrounding metasediements.

(c) The ultramafites are spatially and structurally associated with greenschists (probable metavolcaniclastites) of the Queyfirth unit and therefore may be part of the same magmatic activity (ie. pre-tectonic).

(d) The Queyfirth unit has lithological characteristics which closely resemble the Southern Highland Group (U. Dalradian) of the Grampian Highlands of Scotland (cf. Harris and Pitcher, 1975; Harris et al., 1978) and which are broadly similar to the Dunrossness spilite group (see section 2.6).

2.10 Shetland ophiolite complex

2.10.1 Introduction

The Shetland ophiolite complex occupies the main part of the two most northerly islands of the Shetland archipelago, Unst and Fetlar (Figure 1.2-2), and crops out over a land area of about 110 km^2. The geology of the islands of Unst and Fetlar and surrounding islets is presented in Figure 2.10-1. The complex is partially dismembered and where most complete conforms to the lower part of a model ophiolite pseudostratigraphy (Anon, 1972). This concensus definition of an ophiolite includes, from bottom to top, the following units: tectonite ultramafites, mafic-ultramafic cumulate rocks grading upwards into higher-level gabbros, diorites and plagiogranites, mafic sheeted dykes and mafic volcanics. Associated rocks according to the Penrose definition include an overlying sedimentary sequence, podiform chromite deposits and felsic igneous rocks. Recently, a more practical and expanded definition has been proposed (Moores, 1982). The ophiolite association is expanded in this redefinition to include the following units: a crystalline basement and a shallow water platform sedimentary sequence unconformably deposited on it; a tectonic unit of thrust sheets and/or a melange complex superimposed over the basement; an inverted dynamothermal metamorphic aureole beneath the sole of the ophiolite allochthon and postemplacement deposits. Consideration of this expanded ophiolite association allows a more complete description of the genesis, setting, age and mechanism of emplacement of an ophiolite.

The Shetland ophiolite complex comprises two main allochthonous slices, the upper and lower nappes. The lower nappe attains a thickness of about 6.5 km and gives the most complete section through the ophiolite pseudostratigraphy. The lower nappe on Unst is composed successively of: mantle sequence locally tectonized harzburgite, an ultramafic cumulate sequence, layered and isotropic gabbro, a sheeted dyke complex and metavolcanic rocks.

The basal contact of the mantle sequence harzburgite rocks with the underlying metamorphic basement and melange rocks is marked by *zone* of sheared antigorite serpentinite and steatitized serpentinite. The ophiolitic mantle sequence forms a major portion of the lower nappe on Unst and comprises of harzburgite with minor dunite dykes and lenses and rare pyroxenite dykes. Harzburgite passes upwards, via an interlayered harzburgite-dunite transition zone, into a thick dunite unit, part of the ultramafic cumulate sequence. The cumulus appearance of clinopyroxene in the ultramafic cumulate sequence gives an upward development of a unit dominated by wehrlites and clinopyroxenites showing well displayed cumulus features. The overlying gabbro unit for the most is isotropic, but with cumulus layering locally developed throughout the unit. On the E side of the lower nappe on Unst the gabbro unit is intruded by basic dykes which may constitute the lower portions of a sheeted dyke complex. Also associated with the higher-level gabbro are small intrusive masses and segregations of plagiogranite and varitextured hornblende gabbro. At the highest level in the lower nappe a metavolcanic, or possibly metavolcaniclastic, unit lies with a sharp irregular boundary directly on high-level isotropic gabbro.

The upper nappe is composed solely of mantle sequence harzburgite identical to that of the lower nappe and is similarly antigoritized and sheared at the basal contact. However, unlike the basal antigorite-serpentinite of the lower nappe, rodingite masses occur frequently within basal zone of the upper nappe on Fetlar (Phemister, 1964; Flinn, 1970).

Ophiolitic melange units occur between the upper and lower nappes, below the lower nappe and above the upper nappe (Flinn, 1958 and 1985; Flinn et al., 1979). The melanges consist of mixture of diverse rock types, often highly deformed. A large part of the melange units are composed of graphitic and micaceous mudstones, interbedded with sandstones and gritty sandstones of turbidite affinity (the 'Phyllite group'). These rocks contain tectonic slices or blocks of parautochthonous basement metasedimentary schists and gneisses, ophiolite debris and allochthonous hornblende schist masses. The melange units also contain minor polymict conglomerates which are dominantly composed of gabbro, metavolcanic and various plagiogranite cobble-sized clasts. These conglomerates are believed to be derived, at least in part, from the erosion of the ophiolite nappes. The 'Phyllite group' and polymict conglomerates being deposited on, or in front of, the eroded ophiolite nappes, continued thrusting resulted in them being overridden, deformed and metamorphosed (Flinn, 1958). The status of the vast Funzie conglomerate on the E side of Fetlar is however less clear as it is composed of quartzite clasts of unknown source and has only a small proportion of ophiolitic debris (Flinn, 1956 and 1958). It is also difficult to determine whether the larger ophiolitic blocks within the melange units were introduced by tectonic or sedimentary processes.

The hornblende schists within the melange units are conventionally held to represent exotic tectonic slices of volcanics overidden by the ophiolite nappes. Within the middle melange on Fetlar the hornblende schists are metamorphosed near the basal contact of the overlying mantle sequence harzburgite of the upper nappe. The highest-grade rocks, with garnet-clinopyroxene-brown hornblende assemblages, occur a few metres or tens of metres below the thrust contact and grade downwards into lower-grade rocks with garnet-green hornblende and greenschist-facies assemblages (Spray, 1984; Flinn, 1985). The rest of the ophiolitic rocks and melange units have suffered only low-grade metamorphism, including widespread serpentinization of the ultramafic rocks, prior to find emplacement of the ophiolite nappes.

The direction and amount of displacement on the basal thrust planes is not well constrained, but a ESE-NNW transport direction, ie. approximately orthogonal to the present bulk strike of the complex, is inferred (Flinn et al., 1979). The phyllites within the melange units vary from S-tectonites to L-tectonites with the lineation parallel to variably developed, NNE-SSW trending, minor fold and sheath fold axes. Clasts within the polymict conglomerates of the melange are similarly elongate NNE-SSW, parallel to the strike of the ophiolite complex. The elongation direction of fabrics and minor structures is believed not to parallel the direction of translation of the ophiolite nappes. But, the deformation is the result of constrictional flow of relatively incompetent rock units out sideways towards the direction of easiest relief beneath the relatively rigid ophiolite nappes (Flinn, 1958).

The Dalradian-like metasediments and metavolcanic rocks of the Scatsta division, East Mainland succession (Flinn et al., 1979; Flinn, 1985) constitutes a crystalline basement on which the Shetland ophiolite was emplaced. The timing of ophiolite emplacement has been correlated with a late-stage chloritoid porphyroblast-forming metamorphic episode in the basement rocks (Read, 1934; Flinn et al., 1979; Aziz, 1984). A parautochthonous shallow water platform sedimentary sequence, (cf. Moores, 1982) which may have been unconformable on the basement is not recognised. Formation of the ophiolite is tenatively placed at about 470 Ma (Watson, 1984; Flinn, 1985) with obduction probably occurring very shortly after this time. Ar/Ar dating of the higher grade dynamothermal aureole hornblende schists give ages roughly contemporaneous with many of the unpublished igneous age dates for the complex.

2.10.2 Mantle sequence

2.10.2.1. Harzburgite

The mantle sequence units consist predominantly of a locally tectonized harzburgite (estimated >95% of the total mantle sequence), along with minor dunite and pyroxenite pods and veins. The base of the mantle sequence units is delimited by principal basal thrusts (see section 2.10.8) with the top, where seen, taken as the harzburgite-dunite transition zone (? petrological Moho).

Harzburgite forms the lowest portion of the lower nappe on Unst and the majority of the upper nappe on both Unst and Fetlar (Figure 2.10-1). It crops out in five main occurrences: the lower nappe on Unst in a tract running from Harold's Wick [HP 620 117] down the western margin of the allochthon; the lower nappe at Hamara Field, Fetlar [HU 60 93]; the upper nappe at Clibberswick Unst [HP 65 13]; the upper nappe at Vord Hill [HU 62 93] and at The Heog [HU 65 90], on Fetlar.

The harzburgites of the mantle sequence units generally form rugged topography (eg. Little Heog, Unst [HP 636 112]) with inland exposure varying between 30% to 60%. The harzburgite weathers to a distinctive knobbly, rusty-brown appearance. Bastites after orthopyroxene, tending to be more resistant to weathering, giving the knobbly surface (Figure 2.10-3 and 4).

Basal portions of the harzburgite units are invariably heavily antigoritized in a zone above the basal thrust planes (see section 2.10.8). Above the basal thrust zone of the lower nappe on Unst the harzburgite attains a thickness of up to 2.2 km. More extensive ophiolites commonly possess harzburgite mantle sequences of the order of 5-7 km thick (Coleman, 1977; Smewing, 1981) and may pass downwards into more aluminous lherzolite.

Mineralogically, the harzburgite comprises 74%-92% modal olivine, 7%-26% modal orthopyroxene, 0%-3% modal clinopyroxene and 0.25%-1.5% modal chrome-spinel. The modal analyses were performed on large thin sections and polished slabs (400-2000

mm^2). The term harzburgite used here is strictly applied according to the I.U.G.S. classification scheme (Streckeisen, 1976; Figure 1.3-1), based on the modal proportions of olivine, orthopyroxene and clinopyroxene.

The original minerals of the harzburgite are often pseudomorphed and heavily serpentinized, with 50%-100% alteration common. Multipartite-mesh textured α-serpentine (lizardite) with primary chords defined by magnetite stringers and grains pseudomorphs original olivine. Orthopyroxene is frequently completely altered to α-serpentine (? lizardite) or colourless amphibole giving a bastite pseudomorphs which are bronzy or dark green in hand specimen. Clinopyroxene is more resistant to alteration than the olivine and orthopyroxene, but similar to the orthopyroxene, is pseudomorphed by colourless amphibole and to a lesser extent by α-serpentine. Fresh cores of olivine are forsteritic (about Fo_{90}), the orthopyroxene is enstatite (about En_{91}) and the clinopyroxenes are a chrome-diopside, typically clear and unzoned (Gass et al., 1983; Moffat, unpub. data).

Textures in the harzburgite are very variable. They can be subdivided into three main metamorphic fabric types based on textural-structural features: coarse, mosaic-porphyroclastic and porphyroclastic (nomenclature after Harte, 1977 and 1983). This classification is based around the observation that the phases in ultramafites react to strain at variable rates. Olivine readily recrystallizes under strain usually producing a mosaic of smaller grains (neoblasts). Pyroxene and spinel can less easily relieve strain by recrystallation and tends to respond by fragmentation and, or through, production of internal deformation structures. As a consequence of the differing deformational-mechanical properties two textural distinct microstructures develop: (a) olivine as a granoblastic mosaic, with small (often less than 0.5 mm), strain free, equant or tabular neoblasts; (b) pyroxene porphyroblasts which are coarse (2-10 mm), showing variable strain and may be disrupted and drawn out giving a variety of textural sub-types (ie. disrupted, laminated, fluidal).

The majority of the harzburgites have a coarse-texture (cf. Harte, 1977). Olivine and pyroxenes are strain free with grain sizes between 4 mm and 15 mm. Grain boundaries are mainly smoothly curving but may be straight or irregular. Both olivine and pyroxene may be equant or tabular (Figure 2.10-7a). In thin section these coarse harzburgites appear undeformed but it may be that deformational microstructures have been destroyed by extensive subsequent annealing.

A significant proportion (about 20% of the mantle sequence) of the harzburgites display textures resulting from deformation and recrystallation of the coarse-textured harzburgite. A progressive development from coarse-textures through various deformed textures is observed in thin section, with increasing deformation being accompanied by a marked reduction in grain size and a discontinuous penetrative lamination. Typically, the more tectonized harzburgites show a disrupted-laminated, mosaic-porphyroclastic texture. This consists of coarse-grained (crystal diameters 2-10 mm) orthopyroxene and clinopyroxene porphyroclasts set in finer-grained (crystal diameters 0.3-2 mm) granoblastic mosaic of olivine and orthopyroxene neoblasts. Olivine is not a porphyroclast phase, defining the texture as mosaic-porphyroclastic (Harte, 1977 and 1983). Pyroxene neoblasts can be seen in some harzburgites to form thin laminae (laminated textural sub-type). The pyroxene porphyroclasts are comparable in size with grains in the coarse-textured harzburgite. It is this feature which suggests that the observably deformed mosaic-porphyroclastic harzburgites are derived from the 'undeformed' coarse-type. In a number of mosaic-porphyroclastic harzburgites orthopyroxene porphyroclasts are strained and kinked, with sutured margins. Occasionally, olivine shows a similar 'immature' microstructure consequently the rock is termed a porphyroclastite (Harte, 1977 and 1983).

Alignment of tabular pyroxenes and, or the lamination of disrupted pyroxene defines the penetrative tectonite hazburgite foliation in the field. Black splendent chrome-spinel grain alignment commonly forms a linear component in the tectonite foliation. Parallel to the tectonite foliation a rhythmic modal layering (defined by variations in the respective proportions of olivine and orthopyroxene) is locally developed (Figure 2.10-4 a, b and c). The modal layering appears increasingly well-developed towards the uppermost portions of the mantle sequence (Figure 2.10-2). The layering is laterally inpersistent on an outcrop scale, the modal layers shows no preferential direction of mineral grading, are bilaterally symmetrical and modal layer contacts are often not well-developed (Figure 2.10-4c). The geometrical relations with the tectonite foliation, bilateral symmetry and lack of well defined modal contacts suggest that the rhythmic layering is a metamorphic segregation of olivine and pyroxene rather than primary igneous layering. The sporadic development of the layering in the harzburgite makes it unlikely that it is solely the product of a mechanical segregation accompanying deformation. If that was the case, one might expect some correlation with the style and development of deformational microstructures in the harzburgite; this is not observed. Dick and Santon (1979) outline a modal where phase differentiation accompanies deformation and partial melting of harzburgite. Orthopyroxene undergoes dissolution and precipitation during an incongruent pressure-solution and partial melting process and forms pyroxene-poor and pyroxene-rich layers by the development of high and low strain domains. It is envisaged that a similar mechanism to this produced the modal layering in the mantle sequence of the Shetland ophiolite.

In some outcrops of the mantle sequence harzburgite two tectonite foliations (S_1 and S_2) can be recognised, corresponding to two different ductile shearing episodes (D_1 and D_2), eg. [HP 6451 1083]. Both S_1 and S_2 are wide-spread within the harzburgite though S_2 is the more dominant and best displayed foliation. The first foliation (S_1) has a variable orientation, is usually steeply dipping and often trends at a high angle to the second foliation (S_2). S_2 has a fairly constant orientation over a given area of the mantle sequence units, for example see Figure 2.10-2. Bartholomew (1984) has recently presented an account of the structural and petrofabric data from the mantle sequence harzburgites of the Shetland ophiolite. This work, in particular, describes the mean orientation of the tectonite orthopyroxene foliations and spinel lineations within the mantle sequence units of both Unst and Fetlar. The two tectonite foliation producing events (D_1 and D_2) he regards as being ones of essentially simple shear. The change in D_2 shear sense producing folding patterns in the S_1 plane. In places, eg. Nikka Vord [HU 623 105], the S_1 tectonite foliation is folded into a series of upright E-W trending open folds with approximately horizontal axes. (cf. Pritchard and Neary, 1982; Bartholomew in Gass et al., 1983; Bartholomew, 1984). The S_2 foliation in all the mantle sequence harzburgite units shows a dominantly sinistral shear sense, mean attitude 090/80N and has a slip direction 20/275. With restoration of the harzburgite-dunite transition zone (see section 2.10.2.3) to the horizontal the dominantly *sinistral* shear sense is maintained (Bartholomew, 1984).

2.10.2.2 Ultramafic pods and dykes

A variety of ultramafic pods and dykes cut, or are enclosed in, the harzburgite. These ultramafic bodies comprise (a) dunite pods and lenses; (b) dunite dykes and veins, and (c) rare pyroxenite dykes.

Where not highly deformed pods and lenses of dunite show transgressive relations to the harzburgite foliation (eg. [HP 6467 1227]; Figure 2.10-3b). In places the dunite pods have an irregular form with radiating apophyses 'intruding' the surrounding harzburgite (eg. Hardaberg [HP 6513 1196]). Blocks of harzburgite are also found within some dunite pods. However a majority of the dunite pods and lenses are deformed, oval in plan, usually 1-10 m long, mean length to width ratio ca. 3:1, with well defined sharp margins sub-parallel to the main mantle tectonite foliation (Figure 2.10-3a). The pods and lenses occur throughout the mantle sequence but do tend to form concentrations (Figure 2.10-2) and it may be that individual bodies were structurally linked prior to deformation. However, the upper part of the mantle sequence of the lower nappe on Unst is markedly richer in dunite pods and lenses than the bulk of the mantle sequence (Figure 2.10-2). The tectonite foliation traverses some of the highly deformed dunite bodies, with the foliation defined in the field by a chrome-spinel lineation and discontinuous chrome-spinel laminae (*Figure 2.10-3c*). *Olivine* in these tectonized dunite pods is medium-grained (crystal diameters 1-3 mm), equant, anhedral, strain free, with many grains boundaries intersecting at 120° triple points. In places the pods of dunite form the sites of significant chrome-spinel concentration (? accumulation) within the mantle sequence (eg. [HP 629 112] and [HP 621 102]).

Ultramafic veins and dykes are common at many levels in the mantle sequence harzburgite units, they are discordant, 0.02-1.5 m in width and sharp sided (Figure 2.10-3a and d). Where highly deformed, the dunite veins and dykes run sub-parallel to the tectonite harzburgite foliation and may develop into the lensoid or pod form. Rare, folded and transposed dunite veins are seen (Figure 2.10-4). Similar closed to isoclinal, intrafolial folds of the tectonite foliation of the harzburgite also occur. These folds are interpreted as probable shear folds developed during heterogeneous, ductile, simple shearing of previously discordant dunite veins and are testimony to the high shear strains that developed in the mantle sequence.

Pyroxenite dykes discordant to the main tectonite foliations, sharp sided and undeformed also occur infrequently within the mantle sequence units (eg. GR: [HP 636 107]).

2.10.2.3 Harzburgite-dunite transition zone

The harzburgite-dunite junction is placed at the level of upward disappearance of harzburgite in the ophiolite pseudostratigraphy. Within the lower nappe on Unst the junction crops out and is well-displayed (see Figure 2.10-1 and 2.10-2 for location). Interbanding of dunite in harzburgite increases in frequency over a 20 m section below the junction (Figure 2.10-5a) and possible interfingering or in-folding of harzburgite in dunite is apparent in places (Gass et al., 1983; Bartholomew, 1984). The transition zone phase layers are sub-parallel to the main tectonite foliation in the harzburgite, they have rapidly gradational phase contacts, are between about 0.1 and 2m thick and show no grading (Figure 2.10-5a). Dunite above the harzburgite-dunite junction is intermittently tectonized and is petrographically indistinguishable from the tectonite dunites of the highly-deformed ultramafic pods and dykes within the mantle sequence proper (see section 2.10.2.2).

2.10.3 Ultramafic cumulate sequence

2.10.3.1 Dunite unit

The harzburgite-dunite transition is conventionally interpreted as the junction of the lowest part of the crustal cumulative sequence with the mantle sequence of the ophiolite pseudostratigraphy and is sometimes referred to as the 'petrological Moho' (Moores and Vine, 1971). The 'petrological Moho' marks a significant boundary in terms of the petrological histories of the rocks above and below it, in the cumulative sequence all rocks have an accumulative origin, even though tectonite textures and fabrics may now be present. Below, rocks show evidence of a non-cumulative history, except for perhaps the ultramafic pods and dykes. The dunite unit forms the lowest member of the ultramafic cumulate sequence in the lower nappe of the Shetland ophiolite complex (Figure 2.10-1). The upper limit of the dunite unit of the ultramafic cumulate sequence is marked by the cumulus appearance of clinopyroxene which gives the wehrlite, olivine clinopyroxenite and clinopyroxenite cumulates of the overlying wehrlite-clinopyroxenite unit (see section 2.10.3.2).

The principal exposure of the dunite unit occurs S of the harzburgite-dunite junction, N of Baltasound [HP 63 10], where the unit dips steeply and strikes approximately E-W (Figure 2.10-2). The dunite unit also crops out in an extensive tract running S along the W margin of the lower nappe in central Unst, eg. [HP 60 05]. The thickness of the unit varies between 500 m to over 1000 m N of Baltasound [HP 63 10].

The bulk of the dunite unit consists of massive dunite with an ochreous coloured, smooth weathered surface. Mineralogically, the dunite comprises greater than 95% modal abundance forsteritic olivine (about Fo_{90}) and accessory chrome-spinel. Olivine is typically pseudomorphed by a multipartite mesh α-serpentine, with primary chords and magnetite stringers defining the original grain boundary petrography. Texturally, the dunites comprise two different petrographical/structural groups: (a) those with tectonite textures and foliation; (b) those with cumulus textures. The tectonized dunites show a strong preferred alignment of accessory chrome spinel grains or have 'pull-apart' chrome-spinel laminae (Figure 2.10-5b). These two features help define the tectonite foliation in the field. Olivine grains within the tectonite dunites are mostly unstrained, fine-to-medium-grained (crystal diameters 0.25-1.2 mm), tabular or equant, anhedral and form a granoblastic mosaic. Occasionally olivine remains as a porphyroclast phase producing a porphyroclastic tectonite texture (nomenclature after Harte, 1977 and 1983). The tectonite dunite foliation trends sub-parallel to both the harzburgite-dunite transition zone and local cumulus rhythmic phase and modal layering (Figure 2.10-2). The cumulus dunites lack a strong chrome-spinel alignment. In thin section the olivine texture can look very similar to that of the tectonite dunites but has a medium-grained (crystal diameters 1-2 mm), intergranular adcumulate-like texture. Cumulus rhythmic phase and modal layering of chromitite and dunite is seen in parts of the dunite unit (Figure 2.10-5c) and confirms the cumulative nature of the unit. The localized cumulative podiform bodies of chrome-spinel occur throughout the dunite unit (Figure 2.10-2) and have been commercially exploited in the past as a source of chrome ore (Rivington, 1953; Gass et al., 1983). A detailed account of chromitite distribution, petrography and chrome-spinel geochemistry is given in Gass et al. (1983).

2.10.3.2 Wehrlite-clinopyroxenite unit

The dunite unit of the ultramafic cumulate sequence is overlain by a wehrlite-clinopyroxenite unit. The base of the wehrlite-clinopyroxenite unit is taken as the cumulus appearance of clinopyroxene in the ophiolite pseudostratigraphy, with the top of the unit marked by the cumulus appearance of plagioclase in the overlying gabbro unit. The wehrlite-clinopyroxenite unit is limited to the lower ophiolitic nappe on Unst *(Figure 2.10-1)* and is best exposed along the coastal section between Swarta Skerry [HP 649 079] and Skeo Taing [HP 643 085] (Figure 2.10-2). The unit is also well displayed at Keen of Hamar [HP 646 099], on the S coast of Swinna Ness [HP 637 091] and SW of Uyeasound [HP 587 004]. Within the lower nappe the unit is of very variable thickness ranging between 0-1200 m and extends in a NNE-SSW trending tract through central Unst from Keen of Hamara to a point SW of Uyeasound.

The dunite and wehrlite-clinopyroxenite units appear, in a number of places, to be discordant; for example, N of Keen of Hamar the wehrlite-clinopyrxenite cumulus layering trends ENE-SSW while cumulus layering in the underlying dunite unit trends E-W (Figure 2.10-2). Unfortunately, poor exposure within this area means the possibility that the discordance may be the result of a late tectonic modification of a previously concordant igneous boundary cannot be ruled out.

In terms of gross lithology the wehrlite-clinopyroxenite unit is composed of dunite, wehrlite and clinopyroxenite and is rhythmically layered on a metre to tens of metres scale. The upward continuation of dunite layers into the wehrlite-clinopyroxenite unit means it is often difficult to separate the unit from the underlying dunite unit in the field. For the sake of this description those dunites which occur at a higher-level than the horizon of clinopyroxene cumulus appearance in the ophiolite pseudostratigraphy, are included in the wehrlite-clinopyroxenite unit. The degree of exposure of the unit is variable throughout Unst. Sections through the better exposed areas suggest that the unit comprises approximately 20% dunite, 40% wehrlite and 40% clinopyroxenite.

Mineralogically, rocks within the unit consist of varying proportions of olivine, diopsidic clinopyroxene and chrome spinel. Ca-poor pyroxene is absent throughout both the ultramafic cumulate sequence and gabbro unit. According to the I.U.G.S. classification scheme (Streckeisen, 1976, 1979; Figure 1.3-1), based on the modal proportions of olivine, clinopyroxene and orthopyroxene, the rocks of unit fall within the dunite, wehrlite, olivine clinopyroxenite and clinopyroxenite fields in the olivine-clinopyroxene-orthopyroxene triangle. Chrome-spinel is a ubiquitous accessory phase within the dunites and a frequent accessory in wehrlites and clinopyroxenites. Occasionally, chrome-spinel is a major phase, occurring in places as discontinuous, phase and modal cumulus chrome-spinel ±

olivine ± clinopyroxene layers, eg. Tuvvacuddies, S of Uyeasound [HP 5871 0012].

Olivine is forsteritic ($Fo_{88.3-90.8}$; Table 2.10-3) and is unzoned. The clinopyroxene is a characteristically emerald-green coloured, chrome-diopside (Mg' = 88.7%-95.1%; $En_{46.1-50.0}$: $Wo_{46.5-50.1}$: $Fs_{2.5-6.1}$: Al_2O_3 = 0.52%-5.85%; Cr_2O_3 = 0.35%-1.48%) and is typically clear, unzoned with fine (001) lamellae exsolution intergrowths (Figure 2.10-6d). Within rocks of the unit alteration processes have preferentially replaced olivine to a greater degree than clinopyroxene (Figure 2.10-6b and c). The chrome-diopside is altered in places to a tremolite ± carbonate ± serpentine mineral assemblage. Olivine is mostly pseudomorphed by mesh-textured α-serpentine with accessory talc, carbonate and magnetite. Chrome-spinel is usually unaltered.

The rocks of the unit are identified as cumulates on the basis of textural criteria and by the widespread development of primary cumulus layering throughout the unit.

Texturally, the dunites, wehrlites and clinopyroxenites are typically medium-to coarse-grained (mean crystal diameters 1-10 mm), anhedral- or subhedral- granular adcumulates, or less frequently mesocumulates (Figure 2.10-7 c and d). The adcumulates have little, or no discrete postcumulus material, and mutual interference of cumulus grain boundaries is common. The mesocumulates comprise about 10%-20% by volume of postcumulus material, either as a zoned overgrowth on cumulus crystals or as intercumulus grains, usually clinopyroxene. Rare, poikilitic adcumulates (heteradcumulates) also occur (Figure 2.10-7b). In these rocks coarse-grained, anhedral, unzoned diopsidic clinopyroxene oikocrysts partially enclose subhedral chadacrysts of olivine.

The wehrlite-clinopyroxenite unit is also characterized by ubiquitous cumulus layering, with layers varying in thickness from a centimetre to tens of metres scale. The layers are defined by modal variation in the three primary cumulus phases: olivine, clinopyroxene and chrome-spinel. The three main lithologies of the unit, dunite-wehrlite-clinopyroxenite, frequently form a repeated, macrorhythmic or macrocylic (5-30 m thick) sequences. The base of each rhythm is defined by an horizon where the olivine mode sharply increases. The dunite passes upwards with a thin (20-300 mm), gradational phase contact into uniform or microrhythmically layered wehrlite, which in turn passes up into coarse-grained clinopyroxenite or olivine clinopyroxenite (Figure 2.10-6a and c). The thickness of the rhythmic sub-units and layers within each cyclic sequence vary in an apparently unsystematic fashion. Smaller scale, microrhythmic (20-200 mm), two-by-two layering is intermittent (stratigraphically discontinous) and is best displayed in the wehrlites. Layers and layering are also markedly laterally discontinuous (Figure 2.10-2). Individual phase, modal and grain-size layers of all thicknesses are invariably uniform, mostly with sharp phase, modal and grain-size contacts (Figure 2.10-5d, Figure 2.10-6d). However, rare, thin (20-300 mm wide) gradational contacts do also occur. At one locality (see Figure 2.10-2), wehrlite and clinopyroxenite show complex folding and layer disruption resembling soft-sediment deformation (Figure 2.10-6a, b and c). These features provide supporting evidence that the rocks were formed as a cumulus framework by crystal accumulation processes. The cumulus framework lubricated by intercumulus melt becoming mobilized and deforming in a ductile manner. The deformation may have been triggered by seismic shaking, melt movements, rapid crystal accumulation, temperature or pressure fluctuations associated with melt introduction into the magma chamber system. Infrequently, small blocks of wehrlite (Figure 2.10-6d) and clinopyroxenite occur within the layering and appear to represent fallen blocks or rip-up fragments deposited into or on the cumulus framework.

2.10.4 Gabbro unit

Layered and isotropic gabbros overlie the ultramafic cumulus sequence within the lower nappe on Unst and Fetlar (Figure 2.10-1). The ultramafic cumulate-gabbro unit junction is sharp and poorly exposed along much of its length. The base of the gabbro unit is marked by the appearance of cumulus and intercumulus plagioclase in the ophiolite pseudostratigraphy. The unit is well-exposed along the E coast of Unst from Swarta Skerry [HP 648 080] to Sandwick [HP 627 028], on the E coast of the Muness peninsula [HP 636 018], on the NW coast of Fetlar [HU 595 942] and on the island of Uyea [HP 595 995]. The thickness of the unit is generally between 1 and 2 km.

Rock types within the unit vary from wehrlites, clinopyroxenites, mela-gabbros, to gabbros, through to occasional anorthosites, eg. [HP 6208 0705]. There are coarse-grained rocks of granitoid composition (plagiogranites) which occur at all levels within the unit and lack cumulate features. The basic members which predominate, are variable in grain size and texture, varying from microgabbros to gabbro 'pegmatites'. Many of the coarser varieties are hornblende-bearing and are dioritic in composition. Intrusive breccias are common at higher levels within the gabbro unit, usually with a more-felsic veining of a gabbroic host. Plagiogranites (trondhjemites) occur as veins, dykes and small irregular bodies up to a few metres across. Large stratigraphically and laterally discontinuous masses of wehrlite and clinopyroxenite occur throughout the unit (Figure 2.10-1) and show a gross-scale modal grading from wehrlite (olivine-clinopyroxene cumulate) at the base to clinopyroxenite (clinopyroxene cumulate) at the top. Rhythmic modal layering is developed in both wehrlite and clinopyroxenite.

Layering within the gabbros may be represented by the appearance and/or disappearance of a particular mineral (phase layering), by variations in the proportion of a particular mineral (modal layering) and by grain-size variation (grain-size layering). Layers are invariably thin to medium thick (2 cm-10 cm thick), planar, stratigraphically and laterally discontinuous. However, lensy whispy modal layering is also found, towards the top of the unit, eg. [HP 622 032]. Layer contacts are sharp and modally and grain-size graded layers are rare. Modal layering, with variation in cumulus and intercumulus clinopyroxene and plagioclase, is most frequent.

Mineralogically, the gabbros consist of varying proportions of plagioclase, clinopyroxene and, or hornblende and Fe-Ti oxide. Plagioclase and clinopyroxene are near-ubiquitous cumulus phases. The plagiogranites comprise plagioclase, quartz and minor hornblende. The primary igneous minerals show extensive secondary alteration to greenschist-facies assemblages, with pyroxene uralitized and plagioclase saussaritized. Shear and mylonitic zones within the gabbro unit give a further lithological complexity with a variety of deformed and metasomatised rock types.

2.10.5 Basic dykes

Intruded at a high structural level in the gabbro unit of the lower nappe on Unst are a suite of doleritic and basaltic dykes (Figure 2.10-1). The dykes crop out principally along the E coast of Unst at Knowe of Longawater [HP 637 057], Qui Ness [HP 622 032], Nudda [HP 6232 0395], Pund Stacks [HP 6216 0340], Mu Ness [HP 6381 0130] and on the NW coast of Fetlar at Grodins, near Uriesetter [HP 5990 9386]. Dykes cutting basal antigorite serpentinite have been reported from NE Fetlar (Gass et al., 1983, p 89) and appear to represent a later (? post-syn emplacement) dyke suite. Locally the dykes account for some 50% of the outcrop and for distances of around 10 m cause a 50% extension (eg. Mu Ness and Qui Ness). The dykes are often chilled against the host gabbro, are sub-parallel, vary between 0.5-2.0 m thick and are usually less than 10 m long. Occasionally gabbro apophyses intrude dyke margins suggesting that the gabbro may not have been fully consolidated at the time of intrusion. Along the E coast of Unst the dyke swarms are in places sub-parallel to local phase and modal layering in the gabbro eg. Knowe of Longawater and Nudda. However, modal layering at Qui Ness [HP 6221 0321] trends NW-SE, is near vertical and is cut by the dykes trending vertically NNE-SSW.

The trend of the dykes, which are mostly vertical, is fairly constant at NE-SW to NNE-SSW for all localities on the E coast of Unst.

The dykes have been metamorphosed to the greenschist facies assemblage: albite-actinolite-chlorite-epidote±α-serpentine. A primary aphyric, sub-ophitic petrography is still discernable in most specimens in thin section, but accessory Fe-Ti oxide or chrome-spinel are the only igneous phases remaining.

The dyke swarms are interpreted as being the basal portion of a sheeted dyke complex. In more complete ophiolite complexes swarms of sub-parallel dykes representing between 30%-70% extension pass up into 100% dyke extension, eg. Troodos ophiolite (Wilson, 1959; Gass and Masson-Smith, 1963; Moores and Vine, 1971), Newfoundland ophiolites (Church and Stevens, 1971; Williams and Malpas, 1972) and Oman (Glennie et al., 1974; Rothery, 1983). In these ophiolites early dykes are often split by later ones and a preferred direction of one-way chill is seen, this phenomena has been used to indicate which side of the oceanic spreading axis the dyke swarm represents (Kidd, 1974; Pallister, 1981). The absence of a true sheeted dyke complex in the Shetland ophiolite is not unique, ophiolites from Papua (Davies, 1974) and New Caledonia (Colman and Irwin, 1974) also lack an overlying sheeted dyke complex. Its absence from the Shetlan ophiolite complex is probably due to either erosion and, or, a partial tectonic dismemberment of the ophiolite prior to final emplacement.

Because of the nature of the dyke swarm outcrops, dominantly seen in foreshore sections, there is not indication of the three-dimensional shape of the dyke swarms. Some dykes do pinch out laterally which may suggest that dyke injection occurred by lateral propogation. The frequent chilling of dyke against gabbro clearly indicated they were not fed locally. No dyke root zones as described by Allen (1975) and Rothery (1983) from the Troodos and Oman ophiolites have been recognised.

It is observed that the Shetland ophiolite dyke swarms represent localized areas of up to 50% extension, exactly how this extension is accommodated within the underlying gabbro unit is not clear. If the gabbro was still unconsolidated at the time of dyke intrusion extension may have been accommodated by intergranular slip in the crystal-melt mush. Alternatively, some of the shear and mylonitic zones within the gabbro unit may be concommitant with the oceanic dyke extension event. A third alternative is that dyke intrusion extension was accompanied and accommodated by successive accretion of cumulate layers on the steep walls of the spreading centre magma chamber (cf. Strong and Malpas, 1975; Casey and Karson, 1981). A fourth possibility is that dyke intrusion and consequent oceanic extension was accommodated by tectonic or isostatic subsidence or rotation of the underlying cumulate units during spreading, as suggested by Cann (1974), Dewey and Kidd (1977) in general models and by Girardean and Nicolas (1981) for the Bay of Island ophiolite.

2.10.6 Melange hornblende schists

Hornblende schists and garnet-hornblende schists (eg. 'Norwick Hornblende Schists') occur as blocks and slivers within all three melange units (Figure 2.10-1). Seven main areas of exposure exist: E of the Loch of Watlee [HP 593 048], at Norwick [HP 649 148], in a tract from Wick of Belmont [HP 604 110] to Loch of Stourhoull [HP 578 025], E of Loch of Cliffs [HP 604 110], Houbie, Fetlar [HU 626 905], Aith Ness, Fetlar [HU 632 896] and Virva, Fetlar [HU 644 921]. Thicknesses of the hornblende schist units vary greatly in individual sections (<50-300 m thick) and narrow shear belts and mylonite horizons mark zones of dislocation along the margins. The hornblende schist units are discontinuous and usually surrounded by metasediments which comprising the major part of the melange units beneath the ophiolite nappes.

The rocks are dominantly homogenous, massive, hornblende schists and gneisses, with greenschist-to upper amphibolite-facies metamorphic assemblages developed. Paragenetic assemblages include: chlorite-epidote-amphibole-plagioclase, green or brown hornblende-plagioclase, garnet-brown hornblende-plagioclase, garnet-brown hornblende-clinopyroxene-plagioclase. The highest grade metamorphic rocks, at Virva, NE Fetlar, occur immediately below the upper ophiolite nappe. However, nowhere do the rocks show an intact inverse dynanothermal aureole characteristic of many ophiolite metamorphic soles (Spray, 1984). Original relationships within the metamorphic sole have been obscured by later tectonism. The hornblende schist and gneisses also show minor folding and development of a pronounced tectonite foliation.

The original lithological nature of the hornblende schists is not easy to establish, but the units appear to represent exotic tectonic slices of basic volcanic overidden by the ophiolite nappes. Subsequent tectonism and metamorphism has obliterated all intrusive and/or volcanic features.

K-Ar ages for hornblende schist from the melange range between 465 and 479 Ma (Spray, 1984) and are broadly contemporaneous with formation of the ophiolite (D. Flinn, pers. comm.). The contemporaneous nature of the metamorphic sole and ophiolite igneous crystallization coupled with upper amphibolite-facies sole assemblages is consistent with the notion that obduction occurred while the ophiolite was immature and hot probably in close proximity to the site of formation at an oceanic spreading centre (Spray, 1984).

2.10.7 Other igneous rocks

Igneous, or more strictly metaigneous rocks within the ophiolite complex also include: (a) rodingitized basic rocks which occur within the basal sheared antigorite zones of the upper and lower nappes on Fetlar (Phemister, 1964); (b) gabbro, diorite and plagiogranite blocks and clasts within polymict conglomerate units of various ophiolite melanges (Flinn, 1958 and 1970).

(a) Rodingitized (meta) basic rocks occur skirting the main Vord Hill harzburgite mass on Fetlar: W of Tressa Ness [HU 619 948]; N of Houbie [HU 626 916]; at Swart Houll [HU 643 917] and in a NW-SE trending tract around Urie [HU 593 938]. The bodies are small (<5 m wide) tabular or rounded boudins wrapped by, and elongate in the antigorite tectonite foliation of the basal shear zones. Reaction zones are developed at the contacts between the bodies and the antigorite serpentine and vary in width from several centimetres up to several metres. In many cases, the basic body is completely metasomatized. The rodingite bodies characteristically show evidence of synkinematic brecciation and mylonitization.

Hydrogarnet is characteristic of the rodingites and is commonly associated with diopside, chlorite, tremolite, sphene, epidote, prehnite, idocrase and carbonate. The varying proportions of these minerals, in addition to the differences in intensity of metasomatic replacement and variable deformation state of the rodingite bodies, gives a wide diversity of rock types. Where metasomatic alteration has only mildly affected the basic body a fine-grained subophitic petrography is frequently preserved; with saussuritization of plagioclase and uralitization of pyroxene of the original basalt/dolerite, eg. GR: [HU 601 934].

The rodingitized bodies represent basaltic or doleritic intrusions or tectonic inclusions disrupted and metasomatised in association with shearing and antigorite serpentinization at the base of the ophiolite nappes. The rodingite calc-silicate assemblages probably reflect calcium release during serpentinization of the protolith harzburgite possibly as calcium hydroxide-rich fluids (cf. Barnes et al., 1967; Barnes and Neil, 1971). Reaction between the metasomatic calcium hydroxide fluids and the basalt/dolerite body producing the group of rocks referred to as rodingites.

(b) Gabbro, diorite and porphyritic plagiogranite clasts and blocks of close petrographical similarity to others within main ophiolite nappes occur within polymict conglomeratic units of the middle melange (Figure 2.10-1). Principal localities are at Ramnageo Ness, Unst [HU 624 996], Uyea Island [HU 613 993], Uriesetter, Fetlar [HU 606 936 and HU 607 937], Strongir Holm, Fetlar [HU 597 946], Funzie, Fetlar [HU 66 90] and various sporadic outcrops between Stackabery [HU 614 928] and Tresta [HU 612 905], Fetlar. The conglomerate units vary in thickness from tens of metres to several hundred metres thick, as with the Funzie conglomerate, Fetlar (Flinn, 1956, 1958 and 1970). All are massive, polymictic, clast-supported, with cobble sized clasts set in a sparse, coarse gritty (now schistose) matrix. The clasts include quartzite, gabbro, diorite, quartz-albite-phyric plagiogranite, granophyric plagiogranite and biotite-albite granite. The conglomerate units are strongly deformed, with clasts flattened and elongate NNE-SSW in the main tectonic foliation of the melange rocks.

The conglomerate clasts represent a mixture of detritus derived from the upper portions of the ophiolite pseudostratigraphy and exotic material, eg. the quartzite and biotite-albite granite clasts. The high proportion of 'ophiolite clasts', massive structure, very coarse grain-size and clast supported nature suggest the conglomerates must have been deposited close to the ophiolite nappes. The ophiolite nappes subsequently, during the obduction process, overriding and intensely deforming the conglomerate units.

2.10.8 Basal antigorite-serpentinite

The ultramafic rocks at the base of the two ophiolitic nappes are incompletely serpentinized to an antigorite-serpentinite (Figure 2.10-1). Relic primary minerals and serpentine pseudomorphic textures are invariably altered to a non-pseudomorphing antigorite interpenetrative (bladed-mat) texture (cf. Maltman, 1978; Wicks and Whittaker, 1977). Primary minerals do survive into the antigorite-serpentinite zone, but are rare. Where a pre-antigorite petrography can be observed the antigorite blades are seen as a randomly orientated overprint replacing pseudomorphing mesh textures or as a direct alteration of primary olivine or pyroxene. In some thin sections a patchy distribution of antigorite of different grain size is seen and probably represents alteration after different parent materials. Large blades up to 2 mm long with a preferred orientation denote the sites of previous bastites or primary pyroxene. Similarly, the distribution of magnetite within the antigorite bladed-mat textured serpentinites, best viewed in plane polarized light, defines the outline of previous pseudomorphing mesh structures after olivine.

Close to the basal dislocations of both ophiolitic nappes the random intergrowth of antigorite blades gives way to a schistose antigorite-serpentinite. Here primary petrographic structures are completely overprinted or destroyed. The foliation is defined by a strong prefered orientation of antigorite blades and trails of magnetite grains. These blastomylonitic schistose antigorite-serpentinites are often partially altered, being impregnated with talc or magnesite.

The schistose antigorite-serpentinites also contains lenses of a chlorite-magnetite schist. Where alteration is more advanced (nearest the basal dislocations), the antigorite-serpentinite is in places metasomatized to a talc-magnesite schist (steatite) eg. Queyhouses [HP 615 125] and Cross Geos, Clibberswick [HP 652 122]. Steatite textures from the basal dislocation zones are schistose with talc, magnesite and magnetite stringers defining a penetrative foliation sub-parallel to the basal dislocations. Metamorphic segregation of the various mineral phases giving talc-rich and talc-poor areas within the steatite is seen in the field. A late brittle deformation is often recorded in the steatites with anastomosing talcose shear planes and carbonate cataclastic seams cross-cutting the earlier penetrative foliation.

The basal antigorite-serpentinite zones run alongside the northern and western edges of the lower nappe complex on Unst, the western margin of the Clibberswick block and circumferentially around outliers of the upper nappe on Fetlar (Figure 2.10-1). Minor ultramafic masses within the melange units of the ophiolite complex invariably show non-pseudomorphing antigorite textures both of a schistose blastomylonitic and bladed-mat type.

The shear fabrics displayed by the schistose antigorite-serpentinite, chlorite-magnetite schists and the steatite are the result of shearing stresses developed above the basal dislocations of the ophiolitic nappes. The parallelism of tectonite fabrics to the basal dislocation, indicates high degrees of shear strain and precludes their use in deducing the sense of shear within the zones.

Antigorite growth is widely believed to be pressure dependant (Moody, 1976). Hess et al. (1952) invoked conditions of shearing stress for antigorite growth, a view supported by Francis (1956). However, many workers (eg. Wilkinson, 1953; Moody, 1976) consider thermal conditions to be of importance in antigorite production and have observed primary minerals and pseudomorphing mesh serpentine textures being overprinted during progressive regional metamorphism of serpentinized ultramafic bodies. In the Shetland ophiolite the lack of prefered orientation of antigorite in the bladed-mat textures, exhibited throughout much of the basal zone, tends to preclude antigorite formation purely due to shearing. If pressure was a factor in prompting the random intergrowth of antigorite, it must have been hydrostatic in nature (high pH_2O). It should also be noted that the random intergrowth texture is not merely a static secondary overgrowth of already tectonised antigorite-serpentinite. If thermal conditions were important in antigoritization it is hard to envisage how the thermal effects of a regional metamorphism could be limited to the basal zone of the two ophiolitic nappes. However, if thermal conditions were locally elevated within the basal zones heat could have been derived from two sources: from frictional (shear) heating produced during thrusting, or from hot hydrothermal fluids passing along the basal dislocations.

Shear heating in the region of overthrust faults has been invoked as the dominant heat source for the production of dynamothermal metamorphic aureoles at the base of obducted ophiolites (Graham & England, 1976). Calculations of the maximum amount of heat that could be produced by frictional heating at the base of a moving ophiolite slab (Jamieson, 1979; Malpas, 1979) suggest that increases of 200-300 °C might be expected. This range of temperature increase alone cannot account for the high temperature granulite and amphibolite assemblages developed at the base of many ophiolites eg. Oman (Searle & Malpas, 1980), Newfoundland (Jamieson, 1979) and Shetland (see section 2.10.6). But, it could produce the greater proportion of heat required for antigoritization. Malpas' (1979) calculations are dependent on a number of poorly understood variables. If shearing took place under conditions of high pH_2O at the basal thrust, as seems likely, frictional heating would be reduced and levels of heat production may be a lot lower than the quoted 200-300 °C and insufficient to induce antigorite growth. It should be noted that faults within the ophiolitic nappes eg. between Nikka Vord and Crussa Field, Unst [HP 622 111], also develop quite extensive antigorite-serpentinite zones. These faults record only small displacements and therefore cannot have produced more than low degrees of frictional heating.

The random growth of antigorite (bladed-mat texture) probably developed under hydrostatic conditions, influenced by high-pore fluid pressures (pH_2O) at the base of the nappes. It is likely that these hydrous fluids were heated, and this heat contributed to the antigorite serpentinization. Here antigoritization is probably the result of heated hydrous fluids passing along the fault zone.

The hypothesis that the basal antigorite-serpentinite zones developed under conditions of high pore-fluid pressure (pH_2O) has considerable attraction in the light of current theory on nappe emplacement mechanics (Hubbert and Rubey, 1959; Raleigh and Griggs, 1963; Hsu, 1969; Roberts, 1972). The hydrostatic cushion at the base of the nappe would both lubricate the basal shear and support the overlying dense ophiolitic nappe.

2.10.9 Major and trace element geochemistry

2.10.9.1 Mantle sequence

The refractory nature of the harzburgites is reflected in their highly magnesian bulk compositions (Mg'-values ≈ 90). The harzburgites are extremely poor in CaO (0.22-0.73%), Al_2O_3 (0.13-0.79%), TiO_2 ($\leq$0.02%) and other lithophile elements (Table 2.10-1; Figure 2.10-8). They show very low abundances of incompatible trace elements (Figure 2.10-10) and are rich in compatible trace elements (Figure 2.10-9), with high Ni (1367-2406 ppm), Cr (1842-2367 ppm) and Co (75-124 ppm). Values for these elements are within the range for harzburgites from alpine-type peridotites and mantle sequence harzburgites from other ophiolites (eg. Menzies and Allen, 1974; Colman, 1977; Jaques and Chappell, 1980; Jaques et al., 1983). The harzburgite TiO_2 abundances of less than 0.03% are characteristic of ophiolitic mantle residua from a supra-subduction zone setting (Pearce et al., 1984). Ophiolite mantle residua lithologies from presumed mid-ocean ridge settings are less depleted (TiO_2 $\geq$0.03%). The harzburgites have variable CaO/Al_2O_3 ratios (0.74-1.69), but with a majority of analysed rocks having ratios slightly less than unity.

Mantle sequence dunites have near similar bulk compositions to many of the harzburgites (Mg'-values ≈ 90; Table 2.10-1; Figure 2.10-8). However, the dunites are on average poorer in SiO_2 (40.62-41.58%) and Al_2O_3 (0.03%-0.05%) and richer in MgO (48.3%-48.43%), reflecting an absence of modal pyroxene. Also mantle sequence dunites tend to have significantly lower Ni abundances and higher Cr abundances (Figure 2.10-9), which again reflects an absence of pyroxene and possibly higher abundance of chrome-spinel in the rocks. Dunites within the mantle sequence are geochemically indistinguishable, in terms of major elements, incompatible and compatible trace elements, from both tectonized and cumulate dunites directly above the harzburgite-dunite transition zone within the dunite unit (Table 2.10-1).

2.10.9.2 Ultramafic cumulates

Major and trace elements data for ultramafic cumulates from the dunite and wehrlite-clinopyroxenite units is given in Table 2.10-1 and presented graphically in Figures 2.10-8, 2.10-9 and 2.10-10. Mg'-values for the ultramafic cumulates are uniformally high (≈ 90) and consequently are of little use as an index of fractionation within the dunite and wehrlite-clinopyroxenite units. Compatible elements to the cumulus minerals (eg. Ni, Cr, Co and all major elements except TiO_2, K_2O and P_2O_5) show a variation directly related to the mineral content of the ultramafic cumulate. The overall trend is from Mg-rich (dunite) to more Ca-rich (wehrlite-clinopyroxenite). The behaviour of incompatible trace elements is shown in Figure 2.10-10 by Ti, V and Sr abundances. The ultramafic cumulates show very low abundances of incompatible elements reflecting the predominance of adcumulates within the sequence and the almost complete partitioning of these elements into the coexisting parental melt. The variation in incompatible element abundances seen in the ultramafic cumulates, is again, directly related to modal mineralogy, including the amount of postcumuls material. The proportion of cumulus clinopyroxene, which has markedly higher distribution coefficients for incompatible elements than the other principal cumulus mineral olivine (see Appendix A3), tends to play an important role in determining the incompatible trace element content of the whole rock.

There is a significant change in dunite incompatible trace element geochemistry up into the wehrlite-clinopyroxenite unit. Dunite samples from the wehrlite-clinopyroxenite unit, for example BU419 (64155), BU421 (64837) and BU423 (64156) show higher TiO_2 (0.08%-0.1%) and Zr (6-7 ppm) than those of the underlying dunite unit (Table 2.10-1; Figure 2.10-9). This difference in incompatible trace element content possibly indicates that the parental melt to the dunites of the wehrlite-clinopyroxenite unit were relatively enriched in these elements; the overall up-sequence enrichment of Ti and Zr reflecting progressively more fractionated parental melts. Alternatively, the higher incompatible trace element content may reflect incomplete melt extraction in the higher level dunite cumulates, ie. they may be mesocumulates, although thin section petrography and microprobe analyses (Moffat, unpub data) rule against this idea.

2.10.9.3 Gabbros, diorites and plagiogranites

Principal features of the gabbro major element data are: increased SiO_2 with decreasing Mg'-values; a decrease in Al_2O_3 content with decreasing Mg'-values and near constant CaO abundances (Figure 2.10-8). Compatible trace element abundances vary with the Mg'-value of the rock (Figure 2.10-9). For example, Cr content decreases markedly, consistent with fractionation of spinel and/or clinopyroxene, or is due to variation in modal clinopyroxene content. Ni abundances are uniformally low throughout the gabbros suggesting olivine fractionation was not important. Sr content decreases markedly with differentiation parameters (eg. Figure 2.10-10) *which may* suggest that gabbro parental magma differentiation was controlled by plagioclase fractionation. Abundances of incompatible trace elements (Zr, Y, Rb, Ba, etc) in the gabbros are extremely low, implying almost complete partitioning into, and separation of, the co-existing melt. The variable Ti and V contents of the gabbros are likely to reflect an increased modal abundance of Fe-Ti oxides in the low Mg'-value samples (Figure 2.10-10).

Plagiogranite and diorite major element abundances are shown in Figure 2.10-8. These rocks are characterised by lower MgO and CaO contents and higher abundances of SiO_2 and Na_2O than the gabbros. The variation in MgO with Mg'-value appears to form a continuation of the basic dyke trend. Both the diorites and plagiogranites, in terms of their major element geochemistry, resemble felsic differentiates (plagiogranites) found in other ophiolites (eg. Coleman and Peterman, 1975;

Coleman and Donato, 1979; Size, 1985). All compatible trace element abundances are extremely small (Figure 2.10-9). Incompatible trace element abundances in the diorites, eg. Ti, form a continuation of the gabbro trend when plotted against the Mg'-value differentiation parameter (Figure 2.10-10). The plagiogranite incompatible trace element abundances, plotted against Mg'-value, show a continuation of the trend defined by the basic dykes (Figure 2.10-10). The very low Sr levels confirm the evolved nature of the plagiogranites.

2.10.9.4 Basic dykes and melange hornblende schists

The major and trace element data for the basic dykes is given in Appendix A5 and Gass et al. (1983) and is plotted against the fractionation index 100 Mg/(Mg + Fe^{2+}) in Figure 2.10-8, 9 and 10. The most distinctive major element features of the dykes are a SiO_2 range from 50.31 to 56.06, generally high Al_2O_3 (9.92-19.29%) and Na_2O (1.47-6.05) contents, and dominantly low CaO (6.95-10.51%) and extremely low K_2O (<0.1%) abundances (all oxide percentages quoted are on a volatile-free basis). The highest SiO_2 values exceed the nominal division of 53% between basalts and basaltic andesites. The rocks exhibit a wide range of Al_2O_3 contents and show marked Al_2O_3 enrichment with decreasing Mg'-values, suggesting a lack of plagioclase controlled fractionation. Mg'-values, show a wide range (56.2-78.0). MgO shows a wide dispersion (4.42-18.61%), with a good correlation between Mg'-value and MgO content. Two high-Mg dyke rocks have Mg'-values approaching, or above 70.0 and these are high enough for them to have been in equilibrium with mantle olivine.

Compatible trace element abundances in the basic dyke rocks show a considerable variation (Ni, 28-477 ppm; Cr, 34-1896 ppm; Co, 14-58 ppm), with average Ni, Cr and Co values generally low. Variation in compatible trace element show a good correlation with Mg'-value and MgO content and is consistent with fractionation dominated by olivine and clinopyroxene crystallization. The high-Mg dyke rocks show very high Cr (542 and 1896) and Ni (118 and 477) contents indicating that they have not experienced extensive mafic fractionation.

Incompatible trace element abundances are generally low and variable within the dyke suite, eg. Sr (6-181 ppm), Ba (12-53 ppm), Rb (1-2 ppm), Zr (14-68 ppm), Nb (1-3 ppm), Y (5-19 ppm), TiO_2 (0.13-0.99%) and V (111-225 ppm). Only Sr, Y and Zr show a consistent increase with lower Mg'-values. The constant increase in Sr with fractionation in the dyke suite may also indicated the magmas have not undergone significant amounts of plagioclase crystallisation. Ti and V both show an initial increase wih lower Mg'-values in the basic dyke suite which is followed by a marked decrease at the lowest Mg'-values. This feature probably reflects the presence of Fe-Ti oxide fractionation during the production of the more-evolved dyke rocks. The poor correlation between many of the incompatible trace elements and the fractionation index $100Mg/(Mg + Fe^{2+})$ is probably due to variable secondary mobility of these elements during greenschist facies metamorphic conditions. By analogy with previous studies of element mobility during low-grade metamorphism of basic and intermediate volcanics (Pearce and Cann, 1973; Pearce, 1975, 1978; Wood et al., 1976; Coish, 1977;

Humphris et al., 1978; Hellman et al., 1979; Saunders et al., 1980), it is assumed that the contents of the high field strength (HFS) incompatible trace elements eg. Ti, Zr, V, Y and HREE have remained unchanged during metamorphism. Low field strength (LFS) incompatible trace element abundances need to be interpreted with caution in the light of their probable secondary mobility during metamorphism.

The major and trace element data for the melange hornblende schists is given in Appendix A6 and shown plotted against the fractionation index 100Mg/(Mg + Fe^{2+}) in Figures 2.10-8, 9 and 10. Mg'-values range from 55.3 to 39.8, with an average of about 50.2 for the group. The melange hornblende schists may readily be distinguished from the basic dykes on the basis of their major element composition. Melange hornblende schists are mostly higher in MgO, CaO, K_2O and lower in SiO_2, Al_2O, Na_2O than rocks with a comparable Mg'-value in the basic dykes. The two groups of rocks define separate major element variation trends in Figure 2.10-8. The overall decrease in MgO with lower Mg'-values is suggestive of fractionation involving the crystallisation of mafic mineral phases, eg. olivine and pyroxene. The steady decrease in Al_2O_3 with lower Mg'-values is consistent with plagioclase controlled fractionation.

Compatible trace element abundances in the melange hornblende schists are higher than in the basic dykes for rocks with comparable Mg'-values. Abundances of Ni (96-253 ppm), Cr (127-369 ppm) and Co (23-71 ppm) are typical of values in mid-ocean ridge basalts (cf. Basaltic Volcanism Study Project, 1981). Basic dykes and melange hornblende schists define separate trends when compatible trace elements are plotted against the fractionation index 100Mg(Mg + Fe^{2+}). This clear geochemical separation of the two rock suites suggests they do not possess a single, readily definable common parental magma. Again, the steady decrease in Ni, Cr and Co with decreasing Mg'-values in the hornblende schists is taken as an indication of probable olivine and clinopyroxene controlled fractionation.

Incompatible trace element abundances in the melange hornblende schists, eg. Rb(2-104 ppm), La (7-39 ppm), Ce (8-80 ppm), Ti (0.73-2.51%, hydrous), Zr (70-157 ppm), V (147-529 ppm), Y (23-63 ppm) are mostly considerably higher than in the basic dykes. They are also much higher than typical MORB values, but similar to enriched (E-type) MORB, ocean island and continental tholeiitic basalts (cf. Basaltic Volcanism Study Project, 1981). Ti and V abundances increase with fractionation in the melange hornblende schists and, in contrast with the basic dykes, Fe-Ti oxide controlled fractionation is not indicated. Sr and Rb show no meaningful variation with fractionation. Abundances of these the other low field strength (LFS) elements may well have been affected by secondary alteration processes.

2.10.9.5 Basalt magma type

The problems of correctly classifying altered and metamorphosed volcanic rocks has been discussed by a number of authors (eg. Hart et al., 1974; Humphris and Thompson, 1978). As low-grade metamorphism causes changes in the bulk chemistry of basalts classification of volcanic rocks on the basis of normative mineralogy becomes unsatisfactory. One method of identifying the parentage of basic volcanic is to plot them on a Na_2O + K_2O against SiO_2 diagram (Figure 2.10-11a). It is evident that on this criterion the Shetland ophiolite basic dykes and melange hornblende schists are either alkaline or subalkaline. The basic dykes, however, do all fall in the subalkaline field. The hornblende schists are, on the whole, alkaline.

Figure 2.10-11d is a plot of Na_2O against CaO and shows that Shetland ophiolite basic dykes and hornblende schists generally fall outside the field of average compositions of modern unaltered basaltic rocks (after Stephens, 1980). A number of the basic dyke analyses fall within the spilite fields. The high Na_2O, low CaO character of these samples is thought not to be the *product igneous fractionation processes* but is the result of spilitization (an autometasomatic interaction/alteration of the basaltic melt with seawater).

The influence of secondary processes such as spilitization and low-to medium-grade metamorphism on the original composition of the basic dykes and melange hornblende schists requires that essentially immobile elements (eg. P, Ti, Zr, Y and Nb) are used to indicate magma type. Figure 2.10-11b is a TiO_2 against Zr/P_2O_5 plot for the Shetland ophiolite basic dykes and melange hornblende-schists. The Shetland ophiolite basic dykes and melange hornblende schists fall within, or to the right of both oceanic and continental tholeiitic basalts. Similarly, using the Nb/Y against Zr/P_2O_5 plot (Floyd and Winchester, 1975) which discriminates between alkaline and tholeiitic basalts, all rocks from both suites are clearly tholeiitic (Figure 2.10-11c).

2.10.9.6 Basalt discrimination diagrams

The geochemical discrimination between tholeiitic basalts from different tectonic environments is notoriously difficult (cf. Floyd and Winchester, 1975; Saunders et al., 1980). The problem of geochemical discrimination of Shetland ophiolite basic dykes and melange hornblende schists is compounded by their altered and metamorphosed state. Major element analyses do not reliably reflect the primary geochemistry of the basalts because of the likelihood that selective elemental mobility occurred during the alteration processes. However, selected immobile trace element abundances can be useful in defining the eruptive setting of a basalt (eg. Pearce and Cann, 1971, 1973; Floyd and Winchester, 1975; Winchester and Floyd, 1976; Pearce and Norry, 1979; Pearce, 1980; Alabaster et al., 1982).

Selected trace element discrimination diagrams for Shetland ophiolite complex basic dykes and melange hornblende schists are shown in Figure 2.10.

Basalts from differing tectonic environments have characteristic Zr/Y ratios (Pearce and Cann, 1973; Floyd and Winchester, 1975) and can therefore be useful as a discriminant function. The Zr/Y ratio is believed to reflect the mantle composition, the greater the Zr/Y ratio the more enriched the mantle source (Pearce and Norry, 1979). Figure 2.10-12a is a Zr/Y-Zr diagram in which basic dykes from the upper portion of the gabbro unit of the lower ophiolite nappe fall mainly within the field of island arc tholeiites (IAT). Melange hornblende schists from the ophiolite plot within the compositional field of mid-ocean ridge basalts (MORB) in the diagram.

The Zr/Y-Zr diagram has also been used as a method of describing the petrogenesis of basaltic rocks (Pearce and Norry, 1979; Pearce, 1980; Alabaster, 1982), particularly the level of mantle source heterogeneity (enrichment or depletion). The approach is based on the empirical observation that Zr but not Y is affected by the processes causing source heterogeneity. Consequently, a line drawn at unity through the estimated primordial mantle value will span possible mantle source variation in the Zr/Y-Zr diagram. Modelling geologically reasonable partial melting and fractionation trends in the diagram can then give the character of the mantle source region. Under this approach the basic dykes and melange hornblende schists could be simply linked by a partial melting and fractional crystallisation trend/pathway and be derived from sources of broadly similar composition.

On a Ti-Zr covariation diagram (Figure 2.10-12b) the majority of the basic dyke samples cluster in the field of volcanic arc lavas. A number of samples fall below the arc lava field and emphasises the anomalously low abundances of Ti and other small, highly charged cations (eg. Zr and Nb) in the dyke basalts (see sections 2.10.9.5 and 2.10.9.7), as observed in other arc suites. The melange hornblende schists plot within the MORB field on the Ti-Zr diagram.

The Ti-Zr diagram can also be used to indicate whether an altered or metamorphosed volcanic rock is basic, intermediate or acidic in character (Winchester and Floyd, 1977; Stillman and

William, 1977). It is apparent from the Ti-Zr diagram that the hornblende schist and dyke samples are predominantly basic but that evolved (intermediate) rocks are also present.

The basic dykes and melange hornblende schists are plotted on a Cr-Y covariation diagram in Figure 2.10-12c. This diagram is particularly useful in discriminating island arc tholeiitic basalts (IAT) from mid-ocean ridge basalts (MORB) and within plate basalts (WPB) (Pearce, 1980; Alabaster et al., 1982). In the diagram the immobile compatible element Cr acts as a fractionation index with the abundance of the immobile incompatible element Y being the key discriminant factor. IAT have consistently lower Y abundances than MORB. This observed difference is believed to be a function of the more incompatible element depleted character of the IAT mantle source. In the Cr-Y diagram the basic dykes plot within, or close to the margin of the IAT field. The large variation in Cr abundance between different samples can be attributed to differences in the partial melting and fractional crystallization histories (cf. Alabaster et al., 1982). The melange hornblende schists form a relatively tight cluster within the MORB field, as in the Zr/Y-Zr and Ti-Zr discrimination diagrams.

2.10.9.7 Basalt multi-element diagrams

Multi-element diagrams (spidergrams) are increasingly used to describe chemical variations in basalts from different regions and to identify their eruptive setting eg. Alabaster et al. (1982), Pearce (1983), Saunders and Tarney (1984) and Pearce et al. (1984). Figure 2.10-13 is a multi-element diagram for Shetland ophiolite basic dykes, normalized against an N-type

MORB-value. The rationale behind the elemental ordering used in the diagram and the details of the normative values are given in Appendix A1. The analytical data used in the diagram is given in Appendix A5, with additional data from Gass et al. (1983). It should be noted that the elemental patterns are, in places, incomplete with some trace elements missing from some individual analyses. However, many of the analyses have a comprehensive selection of elements giving adequate and usable patterns. The basic dykes have broadly similar multi-element patterns. Compatible trace elements (Ni, Cr, Co, Sc) abundances show a wide variation from about 0.1 to 7x N-type MORB indicating a variable degree of fractionation of the basalt samples, The high-Mg dyke rock has very high Cr (1896 ppm) and Ni (477 ppm) abundances consistent with the primitive nature of the basalt. Incompatible, high field strength (HFS) elements (V, Y, Ti, Sm, Hf. Zr, P, Nb) form a flat trend which is sub-parallel to the N-type MORB line, but at a much lower level. Incompatible, large ion lithophile (LIL) elements (Th, Ba, Rb, K, Sr) show selective enrichment and depletion relative to N-type MORB. K is depleted in all samples. Ba is moderately enriched in all samples. Th is markedly enriched in the three samples for which it was determined. Th is of particular importance when interpreting this form of diagram because it is one of the few LIL elements which is relatively immobile during submarine alteration and low-grade metamorphism. The other LIL element values are open to suspicion given the uncertainty over their mobility during secondary alteration processes. The LREE (La and Ce) values in two basic dykes (1 and 2 in Figure 2.10-13) are also enriched relative to N-type MORB and it may be that these elements behaved as LIL elements.

The multi-element patterns for the Shetland ophiolite basic dyke rocks are similar to those obtained from tholeiitic basalts from intra-oceanic arc environments (cf. Alabaster et al., 1982; Pearce, 1983; Saunders and Tarney, 1984; Pearce et al., 1984). The low values of incompatible HFS elements is thought to reflect deviation from a mantle source depleted in these elements relative to that of the tholeiitic MORB source. The LIL element enrichment of the basic dykes and island-arc tholeiites (IAT) in general is thought to reflect LIL element enrichment in the depleted mantle source. The LIL elements being selectively transported by an aqueous or siliceous ('subduction component') from a dehydrating subduction slab and introduced into the overlying depleted mantle wedge (Best, 1975; Hawksworth et al., 1977; Saunders and Tarney, 1979).

Geohemical data for hornblende schists from the melange units of the Shetland ophiolite complex is presented in an N-type MORB-normalized multi-element diagram in Figure 2.10-14. Analyses are given in full in Appendix A6. The N-type MORB-normalized geochemical patterns are similar for the majority of the melange hornblende schists from the various melange units. However, the geochemical patterns of these rocks have to be viewed in the light that the rocks have undergone low- to medium-grade dynamothermal metamorphism in the ophiolitic melange. LIL elements and possibly the LREE are likely to have been mobile under these conditions (Saunders et al., 1979; Stern and Elthon, 1979; Humphris, 1983). The garnet-hornblende schist

60369 shows a marked depletion in the incompatible HFS elements (V, Y, Ti) and compatible elements (Ni, Cr, Co, Sc) in the diagram along with enrichment of LREE and LIL elements. These features clearly reflect the evolved character of this sample ($SiO_2\%$ = 64.23). Green hornblende schist 60378 shows a multi-element pattern similar to that of the basic dykes. It has a flat, depleted incompatible HFS element portion, with significant enrichment in LIL elements and LREE (Ce). Other hornblende and garnet-hornblende schists are uniformally enriched in incompatible HFS elements (V, Y, Ti, Hf, Zr, P, Nb) compared with N-type MORB. Nb is enriched to the level of its neighbouring element P and Ce in the diagram. Most LIL elements (Th, Ba, Rb, K) and LREE (Ce, La) show a high degree of enrichment relative to N-type MORB. This LIL element and LREE enrichment may possibly be the result of the mobility of these elements during metamorphism. The level of enrichment however seems to correlate with Mg'-value which may indicate that the LIL element and LREE enrichment is of primary origin. Leaving the LIL element and LREE enrichment aside, the HFS elements can be used to define the petrotectonic environment of the melange hornblende schists. The melange hornblende schists suite contains individual samples of evolved and primitive composition, as indicated by the spread in compatible trace element abundances and Mg'-values within the group. Both evolved and primitive meta-basalts show similar levels of HFS elements thus the observed enrichment of these cannot be attributed to variations in fractional crystallization histories. The melange hornblende schists have multi-element patterns characteristic of continental basalts, ocean island basalts or E-type (enriched) MORB (Alabaster et al., 1982; Pearce, 1983; Saunder and Tarney, 1984; Pearce et al., 1984). The humped patterns are thought to be derived from an incompatible element-enriched mantle source such as associated with 'mantle plumes' (Schilling, 1973; Tarney et al., 1980).

2.10.10 Rare earth element geochemistry

REE analyses are presented in Table 2.10-2 and summarised graphically in Figure 2.10-15.

The mantle sequence tectonite harzburgite AU43 (62961) is characterized by very low REE concentrations (0.05-0.7 x chondrite) typical of depleted peridotites from ophiolites, alpine-type ultramafic bodies and oceanic basement. The harzburgite has a convex-downward (U-or V-shaped) chondrite-normalized pattern which is also characteristic of many ophiolitic, alpine-type and oceanic basement peridotites (see section 4.1).

The cumulate ultramafites show LREE depletion, producing a variably convex-upward patterns at between 0.08-1.5 x chondrite abundance. HREE are flat to slightly enriched compared with MREE. The level of LREE depletion varies within the sample group. Clinopyroxenite BU418 (64152) shows the greatest LREE depletion ($Ce_N/Yb_N = 0.11$). A mineralogically similar cumulate clinopyroxenite BU422 (64153) is much less LREE depleted. Wehrlites BU34 (64149) and BU37 (64129) show a similar moderate LREE depletion ($Ce_N/Yb_N \simeq 0.5$) compared to BU422. This LREE depletion and low total REE abundances is typical of ultramafic cumulates from ophiolites (see section 4.1).

2.10.11 Petrogenesis

2.10.11.1 Mantle petrogenesis

Field evidence places a number of limitations on any petrogenetic interpretation of the mantle sequence.

(a) It is composed mainly of harzburgite, indicating that the degree of partial melting during construction ophiolite was high enough to consume both clinopyroxene and the aluminous phase (garnet, plagioclase or spinel) in the presumed aluminous lherzohite fertile mantle material.

(b) The harzburgites show classic tectonite textures, with possibly two principal shearing episodes represented.

(c) The least refractory residua in the mantle sequence are clinopyroxene-bearing harzburgites.

(d) Olivine fractional crystallisation was prevalent within the mantle sequence following partial melt segregation, as evidenced by the widespread occurrence of dunite pods and lenses.

(e) Rare, minor pyroxenite dykes also point to limited pyroxene fractionation in the mantle sequence.

(f) Podiform chromite bodies occur at all levels within the mantle sequence, with dunite-chromitite phase and modal cumulus layering seen.

The extreme depletion of lithophile elements, high compatible trace element abundances, together with the refractory mineralogy and tectonite fabrics of the mantle sequence harzburgites are consistent with an origin as a mantle residuum after extensive extraction of basaltic melt (cf. Moores, 1969; Himmelberg and Loney, 1973; Menzies, 1976; McCulloch et al., 1981). The predominance of harzburgite, the occurrence of significant chromite pods, low TiO_2 abundances (<0.03%) and overall strongly depleted nature are, more specifically, characteristics of the mantle sequence of supra-subduction zone (SSZ) ophiolites (Pearce et al., 1984) where more advanced partial melting is favoured under conditions of high pH_2O (Hawkesworth et al., 1977).

The mantle sequence harzburgites show a relatively wide range of CaO/Al_2O_3 ratios, but are generally less than unity. This low CaO/Al_2O_3 ratio feature of the harzburgites is hard to reconcile with the fact that the least refractory harzburgites are clinopyroxene-bearing. O'Hara (1968) has shown in the system $CaO-MgO-Al_2O_3-SiO_2$ CMAS, for 'normal' fertile compositions with low CaO/Al_2O_3 ratios that a garnet- or plagioclase-harzburgite (clinopyroxene consumed) residuum is produced at all pressures except 15 Kb, when spinel will melt out first, giving a lherzolite residuum. However, consumption of spinel at around 15 Kb prior to the main mantle partial melting episode would have the effect of raising the CaO/Al_2O_3 ratio of the source. The apparent dichotomy between CaO/Al_2O_3 ratio and mantle sequence mineral content may be evidence for the non-isobaric pseudoinvarient nature of mantle partial melting (Fuji and Scarff, 1986) or may reflect secondary alteration of CaO values during serpentinization.

The variability of CaO/Al_2O_3 ratios in the harzburgites is also problematic, given that it cannot be explained in terms of variable degrees of partial melting at fixed pressure. All magmas generated with a harzburgite or dunite residue will have a fixed CaO/Al_2O_3 ratio that is defined by a 'control plane' within the CMAS system (O'Hara, 1968). One possible explanation is that the variable CaO/Al_2O_3 ratios in the mantle sequence are either an original feature, or are the result of an earlier partial melting event which depleted some portions of the mantle sequence with respect to CaO. An alternative explanation could be that CaO levels in the harzburgites have been differentially affected by secondary alteration processes (serpentinization). However, the lack of any correlation between the degree of serpentinization and the CaO/Al_2O ratio of mantle sequence harzburgites tends to rule against this possibility.

The mantle sequence harzburgites display a U- or V-shaped REE profile, a feature commonly observed in harzburgites and dunites of alpine-type peridotites, ophiolite complexes and ocean basement peridotites (see 4.1). The very low overall REE abundances of the harzburgite is consistent with their presumed mantle residual origin. Similar, U-, V-shaped REE profiles with very low total REE abundances have also been found in ureilite achondrites (Wanke et al., 1972; Boynton et al., 1976). Field, petrographical, mineralogical, major and trace element geochemical features indicate the harzburgites are residual after partial melting of a fertile mantle source. However, consideration of partial melting mechanisms (eg. batch, fractional or disequilibrium melting) and the relevant REE distribution coefficients leads to the conclusion that the U-shaped REE profile cannot represent a simple residuum left after removal of basaltic melt during partial melting of either a chondritic or LREE-depleted mantle peridotite. Melting of 'normal'fertile mantle and basaltic melt extraction will leave a residue severely depleted in LREE and with weak HREE fractionation (Schilling, 1975; Suen et al., 1979; Pallister and Knight, 1981; Frey, 1984). The U-shaped REE profile and implied LREE enrichment of residual mantle harzburgites can be interpreted in a number of ways: (a) as a product of secondary alteration (serpentinization); (b) as a result of cryptic LREE mantle metasomatism, or (c) by sequential integrated disequilibrium partial melting. However, Frey and Suen (1983) and Frey (1984) found no correlation between REE abundances and profile shape with the degree of pseudomorphic serpentinization in mantle sequence rocks and this therefore tends to preclude the first hypothesis. One plausible solution is that the observed LREE-enrichment is developed in mantle residual harzburgites by mantle metasomatism (Hickey and Frey, 1982). Introduction of a geochemically distinct LREE-enriched hydrous fluid phase, possibly from a dehydrating subduction slab, resulting in cryptic metasomatism of the overlying lithospheric mantle wedge. Recently, Prinzhofer and Allegre (1985) have proposed a sequential integrated disequilibrium melting model which accounts for the U-shaped profiles as a natural consequence of continued partial melting during mantle upwelling through the garnet-, spinel- and plagioclase lherzolite mantle stability fields. In this model the U-shaped REE profiles in residual mantle harzburgites is compatible with the LREE-depleted profiles seen in the overlying basic rocks in ophiolite sequences. However, one possible flaw in the model is the adoption of olivine REE distribution coefficients significantly different from other published sets (eg. Appendix A3). The set used by Prinzhofer and Allegre (1985) have LREE and HREE olivine distribution coefficients higher than for the MREE. It is possible that the demonstrated genetic relationship between the mantle residual harzburgite and the ophiolite basic rocks within their model owes much to the rather anomalous olivine REE distribution coefficient set used. However, within the Shetland ophiolite the genetic relationship, on the basis of REE profiles, between the residual mantle sequence harzburgites and the overlying ultramafic cumulates is less problematical. Calculated primitive parental magma(s) to the ultramafic cumulates (see 2.10.11.2) show a degree of LREE-enrichment and thereby seem to require a LREE-enriched source.

The harzburgite-dunite transition zone is considered by most workers to represent a significant petrogenetic boundary (petrological Moho) marking the deepest part of the magmatic cumulate sequence of the ophiolite pseudostratigraphy (eg. Coleman, 1977). In the Shetland Ophiolite some dunites above the transition zone show a tectonite foliation, but in common with many other ophiolite are regarded as cumulates (eg. Christensen and Salisbury, 1979; Prinzhofer et al., 1980; Girardeau and Nicolas, 1981; Cassard et al., 1981) although an ultra-residual origin cannot be discounted.

2.10.11.2 Ultramafic cumulate petrogenesis

The cumulate mineralogy of the Shetland ophiolite defines a distinct crystallisation sequence, with initial olivine + chrome-spinel, then olivine + clinopyroxene ± chrome-spinel and finally clinopyroxene + plagioclase crystallization. Thus, in the ophiolite pseudostratigraphy basal cumulus dunites are followed up-sequence by wehrlites, clinopyroxenites and finally by cumulus gabbros. This order of crystallization corresponds to that of island-arc tholeiites (olivine -> clinopyroxene -> plagioclase) from present oceanic settings (Basaltic Volcanism Study Project, 1981; Pearce et al., 1984) and is consistent with primary magma(s) with a high CaO/Al_2O_3 ratio (O'Hara, 1968). However, as previously seen, the mantle sequence harzburgites have generally low CaO/Al_2O_3 ratios (<1). Primary magma(s) generated in equilibrium with harzburgite or dunite residua have a fixed CaO/Al_2O_3 ratio that is defined by a 'control plane' in the system CMAS and the CaO/Al_2O_3 ratio of the mantle residuum (O'Hara, 1968). Consequently, the Shetland mantle sequence harzburgites would be expected to be residual to primary magma(s) with a low CaO/Al_2O_3 ratio, which in turn would tend to give the crystallization order olivine -> plagioclase -> clinopyroxene; clearly this is not seen in the Shetland ophiolite.

The crystallization order olivine -> clinopyroxene -> plagoclase is observed throughout the ophiolite cumulus sequence, with lenticular wehrlite and clinopyroxene units occurring even at the highest levels of the gabbro unit. This uniformity in crystallization order coupled with a predominance of adcumulates, at least within the ultramafic cumulates, is suggestive of open-system fractionation and steady state magmatic conditions (cf. O'Hara, 1977; Hopson and Pallister, 1980; Smewing, 1981; O'Hara and Mathews, 1981).

The extensive thickness of cumulus dunites and abundance of lenticular dunite pods and veins in the mantle sequence implies extensive olivine fractionation of primitive magma(s) both withn the presumed ophiolitic magma chamber and the underlying mantle. The predominance of cumulus olivine and total absence of cumulus orthopyroxene point to primitive parental magma(s) distinctly undersaturated in silica. Magma oversaturated or saturated in silica may be expected to crystallize orthopyroxene rather than olivine. However, quantitative or semiquantitative estimation of the degree of silica saturation of the primitive parental magma(s) cannot be done since activity-composition relationships for the relevant silicate liquids are presently unknown. The reasons for this undersaturated character of the primitive parental magma(s) and concomitants extensive olivine and chrome-spinel fractionation is not fully understood. One plausible solution is that the presence of a subduction-derived hydrous phase may have expanded the olivine and spinel phase fields, producing extensive olivine and chrome-spinel crystallization. From studies at high pressure of the systems forsterite-diopside-anorthite (Presnall et al., 1978) and forsterite-diopside-quartz (Kushiro, 1969), regarded as useful basaltic analogues, it has been shown that under increasing pH_2O the olivine phase volume expands.

Attempts have been made to model the average primitive parental magma composition for intact ophiolite columns using a mass-balance approach (Elthon, 1979; Pallister, 1984). The ophiolite sequences used have relatively poorly developed ultramafic cumulate units yet give estimated average primitive parental magmas of magnesium basaltic (? picritic or komatitic) composition. Under the assumptions implicit in this kind of model the Shetland ophiolite with an extensive thickness of ultramafic cumulates, would give an estimated average primitive parental magma at least as magnesium-rich as these modelled compositions.

The Mg'-values of primitive magmas parental to the cumulus olivine from rocks of the ultramafic cumulate sequence have been estimated using the experimentally determined equilibrium olivine/melt FeO*/Mg partition coefficient (K_D) of Roeder and Emslie (1970). Olivine behaves with a close approach to thermodynamic ideality, it has a partition coefficient (K_D) relating the Mg and Fe^{2+} content of coexisting crystals and melt which is somewhat independant of pressure, temperature, oxygen fugacity and the bulk composition of the melt (Green and Ringwood, 1967; Roeder and Emslie, 1970; Langmuir and Hanson, 1980). However, the assumption that the K_D is constant may not be strictly valid. Subsequent studies have identified small changes in K_D as a function of pressure and melt composition (eg. Bickle et al., 1976; Bender et al., 1978; Longhi et al., 1978; Leeman, 1978; Ford et al., 1983). Consequently, calculated equilibrium melt Mg'-values given in this section use an FeO*/MgO K_D between olivine and melt of 0.30 and also quote a range of equilibrium melt Mg'-values assuming that K_D varies between 0.27 and 0.33 , ie. $K_D = 0.30 \pm 0.03$.

Mg'-values of melts in equilibrium with cumulus clinopyroxene can be calculated by similar means (cf. Pallister and Hopson, 1981; Elthon and Casey, 1985). The experimentally determined clinopyroxene/melt FeO*/MgO partition coefficient for liquidus clinopyroxene of Grove and Bryan (1983) is used in the calculations (K_D = 0.23 ± 0.02). Again, there is some degree of uncertainty over the exact K_D value applicable. The chosen K_D is at variance with the data of Thompson (1974) and Green et al. (1979) which give an experimentally determined clinopyroxene/melt FeO*/MgO K_D for liquidus clinopyroxene in basalts of 0.29, for widely different temperature and pressure conditions. However, the Grove and Bryan (1983) K_D value is favoured because it is in close agreement with calculated clinopyroxene/melt apparent partition coefficient (K_D') values for a number of ophiolite complexes; the Bay of Islands ophiolite (Church and Riccio, 1977), the Tortuga and Saramiento ophiolites (Stern, 1979) and the Samail ophiolite (Pallister and Hopson, 1981). These apparent partition coefficient values (K_D' = 0.24) were derived from coexisting cumulus clinopyroxene and olivine grains, typically adjacent or nearby grains in the same polished sections. Because of the uncertainties over the K_D value results are given for a range of partition coefficient from 0.21 to 0.25, ie, K_D = 0.23 ± 0.02.

The cumulus mineral data used are given in Table 2.10-3 and the calculated Mg'-values for equilibrium primitive parental magmas appear in Table 2.10-4. The Mg'-value of primitive magma in equilibrium with: (a) cumulus olivine in the adcumulate dunite BU410 (62968) from the dunite unit of the ultramafic cumulate sequence is 66.2 (63.8-68.3); (b) cumulus olivine in the olivine-bearing adcumulate clinopyroxenite BU418 (64152) from the wehrlite-pyroxenite unit is 72.1 (69.9-74.0); (c) cumulus clinopyroxene in adcumulate clinopyroxenite BU418 (64152) is 73.7 (71.9-75.2); (d) cumulus clinopyroxene in adcumuluate clinopyroxenite BU422 (64153) is 74.2 (72.4-75.8); (e) cumulus clinopyroxene in adcumulate wehrlite BU34 (64149) is 73.1 (71.3-74.7); (f) cumulus clinopyroxene in adcumulate wehrlite BU37 (64129) is 74.8 (73.0-76.3). Clearly, the parental magma(s) was highly mafic, with a total range of Mg'-values for equilbrium parental magmas to these selected ultramafic adcumulates of 66.2 to 74.8 (63.8-76.3).

Cumulus mineral trace element data for the same ultramafic cumulate rocks (Table 2.10-3) have also been used to estimate the trace element contents of equilibrium primitive parental magma(s) (cf. Jaques, 1981; Pallister and Hopson, 1981; Elthon and Casey, 1985). Abundances of compatible trace elements Ni and Cr, in cumulus olivine and clinopyroxene respectively give equilibrium parental magma concentration of around 124 ppm Ni and 551 to 687 ppm Cr (Table 2.10-4). The partition coefficients used in the model calculations are given in Appendix A3. The Na_2O content of cumulus clinopyroxene in clinopyroxenites BU418 (64152) and BU422 (64153) (Table 2.10-3), using an Na_2O clinopyroxenite/melt partition coefficient of 0.20 (Elthon and Casey, 1985), give equilibrium parental magma(s) concentrations of 1.79 and 3.0%.

The trace and rare earth element content of the parental magma(s) coexisting with selected ultramafic adcumulates have also been calculated by similar means assuming equilibrium between the bulk mineralogy and melt. The whole rock data used are presented in Tables 2.10-1 and 2.10-2, modal mineral abundances are given in Appendix A6 and the partition coefficients used appear in Appendix A3. The approach used gives a maximum estimate of incompatible trace element abundances and a minimum estimate of compatible trace element abundances (cf. Haskin and Korotev, 1977; Jaques et al., 1983). The modelled equilibrium magma compositions are considered reasonable since the selected cumulus ultramafites are severe adcumulate, containing little or no interstitial melt and have unzoned cumulus phases.

The REE abundances of equilibrium parental magmas to ultramafic adcumulates BU418 (64152), BU422 (64153), BU34 (64149) and BU37 (64129) have been calculated using the olivine and clinopyroxene partition coefficients of Frey et al. (1978, set 5), see Appendix A3. Chondrite-normalized REE patterns for the calculated equilibrium magmas are shown in Figure 2.10-15. The parental magma(s) in equilibrium with clinopyroxenite BU422 (64153) and wehrlites BU34 (64149) and BU37 (64129) have moderately LREE enriched, concave-upwards patterns (Ce_N/Yb_N = 0.81-1.53) with between 1-1.7 x chondritic abundances for the HREE. Clinopyroxenite BU418 (64152) equilibrium parental magma shows a uniform LREE depletion (Ce_N/Yb_N = 0.54) at 7 x chondrite level for the HREE. The modelled REE abundances are considered to be a minimum because the partition coefficients used in the calculations represent maximum values (Frey et al., 1978). The REE patterns of the equilbrium parental magmas are dominantly controlled by the clinopyroxene partition coefficients as this phase is the main repository of the REE. The Ce/Yb ratio of the clinopyroxene partition coefficients used is a maximum value therefore the degree of LREE enrichment in the calculated equilibrium parental magma(s) for BU422 (64153), BU34 (64149) and BU37 (64129) can be taken as a minimum value. Clinopyroxene partition coefficients with lower Ce/Yb ratios will result in higher Ce/Yb ratios in these equilibrium parental magmas. Similarly, the use of clinopyroxene partition coefficients with lower Ce/Yb ratios will give a higher Ce/Yb ratio in the moderately LREE depleted BU418 (64152) parental magma.

Estimated abundances of compatible trace elements (Ni, Cr, Co, Sc) and incompatible trace elements (V, Ti, Zr, Y, Sr) of equilibrium parental magma(s) coexisting with ultramafic cumulates BU410 (62968), BU418 (64152), BU422 (64153), BU34 (64149) and BU37 (64129) are given in Table 2.10-4. Calculated Ni and Cr values using bulk partition coefficients and whole rock data are broadly comparible with those calculated using cumulus mineral data alone. Figure 2.10-16 shows estimated parental magma compositions for the ultramafic cumulates plotted normalised against N-type MORB. Compatible trace element levels are mostly higher than N-type MORB, with incompatible element abundances lower thanN-type MORB. Both elemental groups are at similar levels to concentrations within Shetland ophiolite basic dykes (Figure 2.10-16).

2.10.11.3 Basic dyke and melange hornblende schist petrogenesis

The principal basaltic members of the Shetland ophiolite complex, the basic dykes and the melange hornblende schists, have immobile trace element compositions indicative of a tholeiitic magma type. Both rock suites are dominantly basic, with some intermediate compositions represented.

The basic dyke compositions form a continuous trend on variation diagrams which can be plausibly produced by olivine, clinopyroxene and, in the more-evolved rocks, Fe-Ti oxide controlled low-pressure crystallization differentiation. Effects of plagioclase fractionation are not seen in the basic dyke suite. Primitive high-Mg dykes (Mg'-values = 67.7-78.0) plot at the termination of the fractionation trends on the variation diagrams and consequently may represent parental magma compositions to the more-evolved members of the dyke suite. The high-Mg dykes because of the high-Mg character are potential equilibrium melts with mantle olivine and thereby satisfy one of the fundamental tenets for the identification of primary magmas.

Bulk compositional variation within the melange hornblende schists indicate a possible cogenetic relationship between individual samples which can be explained in terms of olivine, clinopyroxene and plagioclase crystallization differentiation. Fe-Ti oxide fractional crystallization does not seem to be important in the evolution of the suite. However, because of the medium-to-high grade metamorphic nature of many of the rocks analysed, the explanation of observed compositional variation in terms of fractional crystallation should be regarded as highly tentative.

Discrimination diagrams and N-type MORB normalized multi-element diagrams provide strong evidence for the basic dykes being of an island-arc tholeiitic affinity. They show incompatible LIL element enrichment, incompatible HFS trace element depletion and high compatible trace element abundances relative to N-type MORB. The conventional explanation for the cause of the selective LIL element enrichment is that the enriched elements were transported via an aqueous/siliceous phase, from a dehydrating subduction slab into an overlying source zone of mantle melting (eg. Best, 1975; Hawkesworth et al., 1977; Saunders and Tarney, 1979, 1984). The low abundances of HFS elements are probably due to melting of the source which has undergone previous partial melting episodes. The previous melt extraction serves to deplete the mantle source in both LIL and HFS incompatible elements, but continuous LIL element transfer from the adjacent subduction zone results in the LIL element enrichment seen.

The melange hornblende schists plot within the MORB field in discriminant diagrams and have N-type MORB normalized multi-element profiles characteristic of within-plate basalts (continental tholeiite and ocean island basalt) or E-type MORB affinity. The rocks are enriched in most incompatible elements compared with MORB. The degree of enrichment of individual elements shows a direct correlation to the level of incompatibility with a fertile mantle source, ie. the most incompatible elements show the greatest enrichment.

2.10.12 Summary and conclusions

(a) The mantle sequence in the Shetland ophiolite predominantly contains harzburgites. The harzburgites have a refractory mineralogy with the least refractory being clinopyroxene-bearing and display variably developed tectonite foliations. The mantle sequence also contains a signficant proportion of dunite-chromitite pods and veins. These features coupled with the geochemically very depleted nature of the harzburgites (eg. $TiO_2\%<0.03$) are indicative of a residual mantle sequence typical of arc-related supra-subduction zone ophiolites (Pearce et al., 1984). In this type of ophiolite the mantle sequence appears more residual, either having suffered higher degrees of partial melting or melting of a less fertile source, than the mantle sequences of MORB ophiolites. The advanced/secondardy partial melting possibly being influenced by high pH_2O within the sub-ophiolite upper mantle.

(b) The mantle sequence harzburgites show a U- or V-shaped REE profile characteristic of depleted mantle sequence rocks from ophiolites. The mechanism by which a REE profile is produced is not well understood, but two plausible solutions are envisaged, either by sequential integrated disequilibrium partial melting (Prinzhofer and Allegre, 1985) or by cryptic LREE metasomatisim of the mantle sequence rocks, possible by a LREE-enriched fluid phase transferred from an adjacent subduction slab.

(c) Two tectonite foliations are recognisable in the mantle sequence harzburgites of the Shetland ophiolite (Bartholomew, 1984). These can be interpreted in a number of ways, which include production by: two distinct oceanic spreading episodes;

interference of separate spreading centres during the same spreading episode, or as a partial overprinting of an early diapiric mantle upwelling foliation by a subsequent lateral oceanic spreading foliation.

(d) In the Shetland ophiolite basal cumulate dunites are followed up-sequence by wehrlites, clinopyroxenites and gabbros which corresponds to a crystallization order olivine -> clinopyroxene -> plagioclase typical of island-arc tholeiites from present oceanic settings. This again is a characteristic of arc-related supra-subduction zone ophiolites (Pearce et al., 1984). One plausibe explanation for this order of crystallization is that the primitive parental magma(s) generated above subduction zones have intrinsically higher CaO/Al_2O_3 ratios than those from a mid-oceanic setting.

(e) The abundance of cumulate dunite-chromitite bodies within the mantle sequence coupled with the great thickness of dunites within the ultramafic cumulate sequence of the Shetland ophiolite indicates extensive olivine and chrome-spinel fractional crystallisation took place from the primitive (? primary) magma(s). The prolonged olivine and chrome-spinel crystallization can be explained by an expansion of the olivine and chrome-spinel phase volumes under conditions of relatively high pH_2O. Again, such conditions might be expected in a subduction-related magmatic environment.

(f) The uniform crystallization sequence (olivine -> clinopyroxene -> plagioclase) and the predominance of adcumulate rocks in the lower crustal portion of the Shetland ophiolite implies open-system steady state magmatic conditions prevailed.

(g) The predominance of adcumulates and very low abundances of incompatible elements in the ultramafic cumulates suggests near attainment of total equilibrium partitioning of elements during crystallization. Calculations based on an equilibrium crystallization model estimate the primitive parental magma(s) to the ultramafic cumulate sequence contained incompatible trace element abundances considerably lower than N-type MORB (eg. TiO_2 = 0.33-1.0%; Zr = 27-100 ppm; Sr = 19-33 ppm), compatible trace element abundances mostly higher than N-type MORB (eg. Cr = 420-1461 ppm; Ni = 99-279 ppm), low total REE abundances with either a flat shallowly concave-upward or a moderately LREE-depleted REE profile and have low Na_2O concentrations relative to MORB. The estimated equilibrium parental magma(s) were highly magnesium with Mg'-values from 66.2 to 74.8 (63.8-76.3) and as indicated by the absence of cumulus orthopyroxene in the ophiolite probably undersaturated in silica.

(h) Shetland ophiolite basic dykes are depleted in incompatible HFS elements, enriched in incompatible LIL elements and variably depleted and enriched in compatible trace elements relative to N-type MORB. Such features are typical of island-arc tholeiites and further confirm a supra-subduction zone probable marginal basin setting to the ophiolite. Major and trace element variations within the basic dyke suite can be explained in terms of low pressure olivine, clinopyroxene and in the more evolved rocks Fe-Ti oxide controlled crystallization differentiation. Rare high-Mg dykes represent potential parental magma to the more differentiated basic dykes and also satisfy many of the geochemical features of the estimated primitive parental magma(s) to the ultramafic cumulates.

(i) Melange hornblende schists show markedly enriched levels of all incompatible elements (both HFS and LIL) relative to N-type MORB, but plot within the MORB field on discrimination diagrams. Geochemical variation within the suite is consistent with differentiation controlled by low pressure olivine, clinopyroxene and plagioclase fractional crystallization. It is suggested that the suite represents an early period of E-type MORB magmatism and may be remnants of the pre-arc spreading oceanic lithosphere. Formation of this magmatic suite may have been responsible for depletion of the mantle sequence prior to the marginal (fore- or back-arc) basin extension event which produced the main Shetland ophiolite sequence.

2.11 Ultramafites within the Quarff tectonic melange

2.11.1 Geological setting

The Quarff tectonic melange and metamorphic succession forms a separate tectonostratigraphic unit to the E of the East Mainland succession (Figure 1.2-2). The tectonic melange occurs as a complex, ca. 1 km wide, ca. 16 km long, N-S trending, arcuate fault zone extending from Rova Head, GR: [HU 46 45] in the N to Fladdabister, GR: [HU 43 31] in the S. The tectonic melange comprises fault-bounded slices of allochthonous and parautochthonous rocks and separates the parautochthonous Quarff succession from the Dunrossness phyllitic and Clift Hills phyllitic groups of the Clift Hills division, East Mainland succession (cf. Flinn, 1967 ; Flinn et al., 1972). The melange zone is cut and offset dextrally by the Neugal Water fault and is unconformably overlain by M. Devonian (Givetian) ORS sediments, which dip E away from the zone. In places, however, the tectonic melange is faulted against, and lies subparallel to, the W margin of the M. Devonian ORS. A probable splay of the tectonic melange fault zone truncates ORS sandstones E of Aith Wick, near Cunningsburgh and defines the eastern margin of the Dunrossness spilite group (see section 2.6).

The Quarff parautochthon, E of the tectonic melange, comprises a metamorphic succession similar in many respects to that of W of the tectonic melange (cf. Flinn, 1967). From bottom (W) to top (E) the succession is: (a) partially veined, migmatitic pelitic gneiss and gneissose semipelitic, and psammitic granulites (equivalent of the Colla Firth group, Whiteness division of the East Mainland succession);

(b) micaceous semipelitic and psammitic granulites, with subordinate calc-silicate granulite and crystalline limestone (equivalent of the Wadbister Ness group, Whiteness division of the East Mainland succession; the equivalent of the Girlsta Limestone is absent);

(c) crystalline limestone (equivalent of the Laxfirth Limestone, Whiteness division of the East Mainland succession);

(d) massively-bedded, arkosic 'gritty' psammites and calcareous 'gritty' psammites (the Fladdabister grits, with no correlatable equivalent lithology W of the Quarff tectonic melange).

A K-Ar whole-rock date of 454 ± 28 Ma from the Quarff parautochthon is similar to metamorphic cooling ages from the East Mainland succession (Miller and Flinn, 1966).

The Quarff tectonic melange is generally poorly exposured and comprises parautochthonous masses derived from the adjacent metamorphic successions (eg. Dunrossness phyllitic group rocks and ?Laxfirth Limestone) and possible allochthonous lithologies. The tectonic melange disrupts the main regional metamorphic foliation, both in the adjacent metamorphic rocks and the enclosed parautochthonous metamorphic rock masses. Black, impure, fine-grained limestones and very pure, white metasedimentary quartzites in the Quarff tectonic melange have no correlatives within either the autochthonous East Midland succession or the Quarff parautochthon. The major part of the melange consists of black to dark-grey, pelitic phyllites, best exposed on the coast at Bight of Vatsland, near Rova Head (eg. GR: [HU 4688 4520]). At this locality mylonitized, black and dark-grey pelitic phyllites crop out on the foreshore and display a complex array of NE-SW trending anastomosing shears/faults with multiple fabric development and late, brittle, cataclastic breccia seams. The pelitic phyllites are graphitic in places and locally show a sinistral shear geometry, however, the relative movement direction for the tectonic melange as a whole is unknown. The multiple mylonite/ cataclastic fabric development seen in the field is also observed in thin section with the mylonitic foliation(s) generally overprinted by late, brittle dislocations (Figure 2.11-1a and b).

Heavily altered, minor, ultramafite tectonic slices occur at three localities within the *Quarff tectonic melange (Figure* 1.2-2): (a) at Severs Dale, GR: [HU 4224 3760]; (b) at Madwell, GR; [HU 429 331], and (c) at Fladdabister, GR: [HU 431 320].

2.11.2 Details of exposure

2.11.2.1 Severs Dale ultramafite

The ultramafite occurs in an isolated stream section at Severs Dale, NNW of Ward of Virdalee, S Mainland. Dark-green coloured, partially steatitized antigorite-serpentinite is exposed at GR: [HU 4224 3760] and is associated with quartz-carbonate mylonites with relic ?chrome-spinel grains. Tectonized lenses of crystalline limestone, massive quartzite, calcareous 'gritty' psammite and mylonitized, black-grey, pelitic phyllite crop out in close proximity to the ultramafite (eg. GR: [HU 4224 3778]). Locally, the mylonitic foliation and anastomosing dislocation planes trend NNE-SSW (044° - 006°) and dip E (25-70°).

2.11.2.2 Madwell ultramafite

The Madwell ultramafite crops out in a stream section about 1 km NW of Fladdabister at GR: [HU 429 331]. Green-grey, partially steatitized (carb-rich), antigorite-serpentinite occurs as a ca. 10 m wide, phacoidal, tectonic mass. Also exposed in the stream section are other lithologies typical of the tectonic melange, including: mylonitized black pelitic phyllite, white metasedimentary quartzite, micaceous crystalline limestone with quartz segregations and closely laminated quartzose psammite (eg. GR: [HU 4296 3313].

2.11.2.3 Fladdabister ultramafite

The Fladdabister ultramafite forms the largest ultramafite mass in the Quarff tectonic melange and is exposed 50-100 m E of the main A970 road, between Burn of Nugarth, GR: [HU 4312 3200] and Burn of the Scord, GR: [HU 4308 3223]. Mylonitized antigorite-serpentinite and steatitized (carb-rich) antigorite-serpentinite occurs as discontinuous, phacoidal, tectonic slices. The altered ultramafites show a metamorphic differentiation into carbonate-rich and serpentine-rich domains and the foliation dips steeply W and strikes NNW-SSW, parallel to the margins of the Quarff tectonic melange. The contact between ultramafite and the enclosing mylonitized, grey, pelitic phyllite is seen at GR: [HU 4312 3200].

2.11.3 Petrography and geochemistry

Petrographical and mineralogical features are broadly similar in all three ultramafite masses. The more-massive, tectonized, serpentinized ultramafites show non-pseudomorphic, interpenetrative (bladed-mat) to schistose, γ-serpentine and serpophite textures. The mylonitized altered ultramafites consist of γ-serpentine + carbonate ± quartz ± talc; grains of which are elongate, disrupted, subgrained and kinked. Parallel to the mylonitic foliation carbonate-rich and carbonate-poor steatite/antigorite-serpentinite domains are frequently developed. Also coarse (grain size = 0.5 - 1.5 mm), magnetite grains (probably after chrome-spinel) may occur disrupted in the mylonitic foliation (Figure 2.11-1c). Frequently, such magnetite grains are the only petrographic indication of the ultramafic affinity of some of the carbonate-quartz mylonites. Early, more-ductile, mylonitic foliations are cross cut by cataclastic seams and chlorite or carbonate or γ-serpentine granular veins.

Table 2.2-1 contains whole-rock major and trace element data for steatitized antigorite-serpentinite BGB6 (64130) and talc-carbonate mylonite BM11 (64123) from the Fladdabister ultramafite (GR: [HU 4311 3204] and GR: [HU 4312 3201] respectively), and carbonate-quartz mylonite BM38 (64132) from the Severs Dale ultramafite (GR: [HU 4224 3761]). All three rocks have high Mg′-values (83.7 - 89.8), but show a wide variation in major element abundances (eg. MgO = 16.42 - 38.65%; SiO_2 = 48.08 - 56.68%; Al_2O_3 = 0.37 - 4.74%; CaO = 0.28 - 14.98%). Compatible trace element abundances are uniformally high (eg. Cr = 1529 - 2602 ppm; Ni = 1052 - 1962 ppm; Co = 69 - 118 ppm); incompatible trace element abundances are uniformally low (eg. Sr = 55 - 87 ppm; Zr = 2 - 6 ppm; Y = 3.8 - 17.2 ppm). Ce and Nd abundances in BGB6 (64130) and BM38 (64132) are greater than chondrite (Ce_N = 1.43 and 6.35, Nd_N = 1.96 and 8.80, respectively) and show moderate LREE to MREE depletion (Ce_N/Nd_N = 0.73 and 0.72).

2.11.4 Summary and conclusions

(a) The relative movement direction of the Quarff tectonic melange is unknown, although, locally, mylonitic fabrics suggest a sinstral strike-slip geometry and the zone appears to cut up-sequence from N to S.

(b) The predominance of brittle, calcaclastic and low-grade (?greenschist), mylonitic fabrics supports a high-level origin for the tectonic melange. The tectonic melange clearly disrupts previously deformed and metamorphosed rocks of the adjacent Clift Hills division, East Mainland succession and Quarff parautochthon and therefore probably post-dates the ca. 490 peak of metamorphism identified in Dunrossness spilite group rocks (see section 2.6).

(c) The Quarff parautochthon and tectonic melange are unconformably overlain by M. Devonian (Givetian) ORS sediments, therefore, emplacement occurred prior to about 380 Ma (using the timescale of Harland et al., 1982). However, in places ORS sediments are truncated by faults associated with the tectonic melange and suggest the zone has been reactivated after Devonian times.

(d) The tectonic melange contains a number of lithologies not identified in the metamorphic successions to the E and W of the zone, notably massive, white, metasedimentary quartzite and blakc, impure, fine-grained limestone. However, the main part of the tectonic melange is composed of mylonitised, black-grey, pelitic and semipelitic phyllites are indistinguishable from metasedimentary units within the Dunrossness spilite group. Also ultramafites with the Quarff tectonic melange are geochemically similar to Dunrossness spilite group ultramafites (see section 2.6). It is possible, therefore, the tectonic melange dominantly consists of parautochthonous rocks.

(e) Ultramafites within the Quarff tectonic melange are variably steatitized. Consequently, geochemical features of the rocks should be view in the light that secondary mobility and fractionation of major, and trace and rare earth elements may have occurred. Nevertheless, the major and trace element data are consistent with a peridotitic protolith with an olivine ± pyroxene ± chrome-spinel mineral assemblage. High compatible and low incompatible trace element abundances indicate a possible peridotitic cumulate or restite. Ce and Nd abundances in the altered ultramafites suggest they are LREE-depleted relative to MREE, with overall REE abundances greater than chondrite levels. These REE profile characteristics are found in some Layered complex ultramafites, Oceanic picrites, Boninites and some Peridotitic komatiites (see section 4.1).

3. Ultramafites within calc-alkaline plutonic complexes of the Shetland Caledonides

The aims of this section are:

(a) to present a review of the occurrence, age relations, petrology and geochemistry of ultramafites associated with calc-alkaline plutonic complexes in Shetland;

(b) to establish, primarily from the internal structure and petrography of the ultramafites, their mechanism of emplacement;

(c) to investigate the petrogenesis of the ultramafites, and

(d) to test the petrological consanguinity of the ultramafites and other units of the relevant plutonic complex.

3.1 Ultramafites within the Brae plutonic complex

3.1.1 Geological setting

The calc-alkaline Brae plutonic complex occupies approximately 5.4 km^2 of the S.W. peninsular of Delting, central Mainland, to the S of Sullom Voe (Figure 1.2-2). The main outcrop is centred around Brae village, with satellite bodies S of Olna Firth (Figure 3.1-1). The several compact, composite, stock-like intrusions cross cut and contact metamorphose Yell Sound division (Moine-like) and Scatsta division (Dalradian-like) rocks of the East Mainland succession. The main intrusion is truncated on the western margin by the Walls Boundary fault.

The calc-alkaline suite comprises a plutonic ultramafite-gabbro-diorite-granodiorite-granite association. The complex is composed of plutonic rocks of a wide compositional range (ca. 40 - 70 wt% SiO_2) and lithological diversity, which contains combinations of olivine, Ca-poor pyroxene, Ca-rich pyroxene, hornblende, biotite, plagioclase, alkali-feldspar and quartz. Emplacement of younger granitic and dioritic magmas in the same igneous locus giving increased scope for variability. These factors tend to hinder adequate generalization, however, the following is a summary of lithologies represented in the Brae plutonic complex (nomenclature according to Figure 1.3-1).

(a) Ultramafites: dunite, wehrlite, olivine clinopyroxenite, lherzolite, olivine websterite, websterite, biotite-websterite, biotite-olivine websterite, hornblende-olivine websterite, amphibolized websterite, hornblendite.

(b) Gabbros: gabbronorite (orthopyroxene gabbro), hornblende gabbronorite (hornblende-orthopyroxene gabbro), amphibolized gabbronorite, hornblende gabbro, biotite-hornblende gabbronorite.

(c) Diorites: biotite-two-pyroxene diorite, hornblende-biotite-two-pyroxene diorite, hornblende-biotite diorite, hornblende diorite, amphibolized biotite-two-pyroxene diorite, biotite-magnetite-two-pyroxene diorite.

(d) Granitic leucocratic rocks: biotite-hornblende tonalite, two-mica tonalite, biotite granodiorite, biotite granite.

(e) Granitic pegmatites, aplites and minette lamprophyres.

The plutonic complex can be divided into a number of distinct mappable lithological units (order according to apparent relative age).

(a) Satellitic masses of clinopyroxene-rich ultramafite, with subordinate dunite, the largest of which lies at Wetherstaness (Figure 3.1-1).

(b) Widespread marginal-facies, xenolithic, two-pyroxene diorite and gabbronorite, containing altered country rock gneisses and ultramafites, particularly well developed along the eastern margin of the main outcrop at Mill Loch (Figure 3.1-1).

(c) A main biotite-two-pyroxene diorites and hornblende-biotite-two-pyroxene dioriteunit(s), extensively amphibolized in places.

(d) Hornblendite, hornblende gabbro and hornblende diorite, chiefly represented to the S of Olna Firth (Figure 3.1-1).

(e) Granitic leucocratic rocks, chiefly consisting of tonalite and granodiorite sheets cross cutting the main diorite masses.

(f) Granitic pegmatites, aplites and minette lampropyre sheets.

3.1.2 Age constraints

Field and radiometric data suggests that the Brae plutonic complex is a late- to post-tectonic Caledonian pluton intruded at about 430 Ma (early Silurian; using the time scale of Harland et al., 1982). The critical observations in support of this conclusion are the following.

(a) The pluton clearly cross cuts the NNE-SSW trend of the regional metamorphic foliation in the East Mainland succession (Figure 1.2-2). Xenoliths of country-rock schists and gneisses are abundant in some units of the plutonic complex (eg. Figure 3.1.5a and b). Both xenoliths and country rock show evidence of moderate- to low-pressure, high-temperature contact metamorphism. Radiometric dating of the adjacent Collafirth migmatite belt gives an Rb/Sr muscovite age of 526 Ma (Flinn and Pringle, 1976) for a pre-Brae plutonic complex migmatitic event within the East Mainland succession. This data gives a reliable maximum possible age for the intrusion of the Brae plutonic complex of about 526 Ma.

(b) Units within the plutonic complex are cut by mylonitic shear zones and the complex as a whole is truncated on the W by the Walls Boundary fault. The features indicate the complex, although post-dating the main tectonometamorphic episode(s) affecting the East Mainland succession, has suffered extensive late fault/shear zone tectonism.

(c) K-Ar radiometric dates for two rocks from the plutonic complex, a 'hypersthene diorite' from Burravoe Houb and a biotite-two-pyroxene diorite from E of Mill Burn give ages of 390 Ma (Flinn, pers. comm. in Gill, 1965) and 433 ± 6 Ma (Gill, 1965) respectively. The younger of these ages may have been affected by partial Ar loss and resetting.

(d) A hornblende-separate sample from hornblende gabbro AB15 (62938) from a satellite intrusion S of Olna Firth at the Loch of Gronfirth, GR: [HU3829 6245] gives a $^{40}Ar/^{39}Ar$ plateau age of 427 ± 8 Ma. The $^{40}Ar/^{39}Ar$ step age data is given in Table 3.1-1 and presented graphically as an age spectrum in Figure 3.1-7a. Steps 5, 6 and 7, containing over 80% of the ^{39}Ar, were used in the plateau age calculation. Both methods for calculating the plateau age are in close agreement and are supported by isochron age calculations (Figure 3.1-7b and c). The four initial steps of the age spectrum show anomalously old ages indicative of late excess argon contamination of the rock and result in a total fusion age (440.7 Ma) significantly older than the plateau age (cf. Harrison and McDougall, 1981).

Age relations between the different units of the plutonic complex are very difficult to determine given the relatively poor inland exposure and the multi-intrusion history, involving possible hybridization and assimilation. Xenolith-host relationships and minor intrusive contacts are scarce. Nevertheless, age relations between the granitic rock suite and the other plutonic units which comprise the Brae plutonic complex consistently indicate that the granitic rocks are younger. The field relations suggest that emplacement of the ultramafite and marginal-facies, two-pyroxene diorite and gabbronorite units mostly pre-date the main diorite units.

3.1.3 Details of exposure

3.1.3.1 Gronfirth Runie ultramafite

A ca. 10 m wide, ca. 400 m long, N-S trending (strike 178°) dyke of massive serpentinized peridotite crops out W of Loch of Gronfirth, GR: [HU 380 625] (Figure 3.1-1). The dyke intrudes Scatsta quartzitic group rocks of the Scatsta division, East Mainland succession and is slightly discordant to the country-rock foliation. Parallel to the margins of the intrusive body is a variably developed preferred alignment of pyroxene or pseudomorphed pyroxene grains. The pyroxene alignment is in places (eg. GR: [HU 3805 6240] cross cut by minor dunite veins suggesting that the foliation is a possible igneous lamination.

3.1.3.2 Grobsness ultramafites

Two ultramafite bodies crop out in the Grobsness area, S of Olna Firth (Figure 3.1-1).

(a) A 20-30 m wide, > 200 m long, NW-SE trending (strike 139°), massive serpentinized dunite and peridotite dyke is exposed on the NW slope of the Hills of Grobsness at GR: [HU 3731 6342]. Large ultramafite boulders below the exposures (eg. GR: [HU 3725 6342]) show phase and modal cumulus layering, with microrhythmic (< 10 cm thick), parallel layers of serpentinized dunite and pyroxene-rich peridotite. The dyke intrudes the Scatsta pelitic group, Scatsta division, East Mainland succession.

(b) Centred around Grobsness, GR: [HU 369 635] is a poorly exposed, discordant mass of amphibolized pyroxenite (Figure 3.1-1). The ultramafite is best exposed on the foreshore section. However, even within this section relations with the country rock are unclear. The northern contact of the ultramafite is truncated by a ca. 30 m wide band of mylonitized and veined country-rock gneissose schist and the southern margin is intruded by a minette lamprophyre dyke.

3.1.3.3 Sneugie ultramafite

The Sneugie ultramafite consists of a small, isolated outcrop of steatitized antigorite-serpentinite. Two small (< 5 m across) exposures of ultramafite lie approximately 20 m apart on the northern slopes of Sneugie, S of Olna Firth, GR: [HU 386 635] (Figure 3.1-1) and are entirely surrounded by units of the Scatsta quartzitic group, Scatsta division, East Mainland succession.

3.1.3.4 Wetherstaness ultramafite

The most extensive of the ultramafite masses within the Brae plutonic complex crops out in the Wetherstaness area (Figure 3.1-1). The ultramafite is poorly exposed inland, but in good coastal exposure it is possible to see that the rocks are composed mainly of clinopyroxene-rich (cpx > opx) pyroxenite and peridotite, with minor dunites. For the purpose of mapping (cf. Figure 3.1-2) rock types have been divided into three units: dunites, peridotites (which strictly include wehrlite and lherzolite), and pyroxenites (which strictly include websterite, olivinve websterite and olivine clinopyroxenite). The ultramafites may have ± biotite ± hornblende ± chrome-spinel ± Fe-Ti oxide as accessory phases. Clinopyroxene-rich pyroxenites make up about 75% of the ultramafic mass; peridotite about 20%, and dunite about 5%. The clinopyroxene-rich ultramafites commonly form massive, blocky exposure characterised by a knobbly, pyroxene-studded, brown-ochre crust. Cumulus layering features are scarce (eg. GR: [HU 3574 6520]. However, preferred orientation of pyroxene is common. The pyroxene foliation is occasionally cross cut by later ultramafite veins and dykes and is therefore thought to represent a magmatic flowage feature (igneous lamination). The intense, penetrative, tectonite foliation characteristic of many Alpine-type complex or Ophiolite complex mantle sequence ultramafites is absent. In a few exposures modal layering is apparent, but is not well defined and is stratigraphically discontinuous. Contacts between pyroxenites and peridotites are typically gradational. In contrast, the dunites and some wehrlites form elongate masses or small, anastomosing, irregular dyke-like bodies that may have sharp or gradational contacts with surrounding pyroxenite and peridotite. The anastomosing dunite or wehrlite dyke-vein systems are seen locally to grade into igneous breccia with pyroxenite or peridotite blocks. The widespread distribution of the brecciated pyroxenites and peridotites is shown in Figure 3.1-2. Brecciated websterite is best exposed in the coastal section S of Wetherstaness (eg. GR: [HU 3577 6509]) and at Skull point (eg. GR: [HU 3514 6528]). S of Wetherstaness (Figure 3.1-2) thin, irregular, anastomosing dunite veins and dykes disrupt the massive websterite and olivine websterite (eg. Figure 3.1-3a). The dunite is frequently ladened with variable sized and irregular shaped fragments of pyroxenite. In the central parts of the wider dyke-vein systems small pyroxenite fragments may form upto 50% of the rock; the resultant ultramafite sometimes resembles massive wehrlite or lherzolite (Figure 3.1-3b). The fine-scale nature of some of the dunite veining is best seen in polished slabs (eg. Figure 3.1-3c), where massive pyroxenite is disrupted by seams of partially serpentinized, fine-grained olivine. The anastomosing dunite dyke-vein system grades into partially brecciated pyroxenite with dunite 'fingers' projecting into more massive pyroxenite. Frequently associated with the developing brecciation is a marked grain-size increase (Figure 3.1-3c) and probably indicates that recrystallization or continued crystallization of the pyroxenite took place induced by the brecciation event. Some veins show an undisturbed continuity of the contacts of spatially associated pyroxenite blocks across intervening dunite. This feature suggests that significant dilation and block transportation has not occurred. In some areas of brecciation pyroxenite fragments develop a preferred orientation in the sparse dunitic or wehrlitic matrix suggestive of flow alignment after mechanical disruption of the pyroxenite or peridotite (eg. Figure 3.1-3d).

Within the foreshore section S of Wetherstaness (Figure 3.1-2, location A) occur small (generally < 1 m across), randomly orientated and distributed areas of Cu-Ni-Fe sulphide-bearing websterite and olivine websterite. These sulphide-bearing pyroxenites are seen as rusty-red oxidised areas, with transitional margins, within the massive pyroxenite. The proportion of sulphide to silicate phases is generally low (< 40%) and in many areas the disseminated sulphides are only an accessory phase.

Contacts between the Wetherstaness ultramafite and other units of the Brae plutonic complex are poorly exposed. To the N of Skult point (Figure 3.1-2) the junction of ultramafite and marginal-facies diorite appears to be a partially fault modified igneous contact. SW of Wetherstaness (Figure 3.1-2, location B) an isolated mass of richly-xenolithic marginal-facies diorite (Figure 3.1-5a and b) overlies brecciated pyroxenite and pyroxene-rich peridotite in the cliff section; the contact is sharp and again partially fault modified. At both localities relative age relations are not discernable as zones of mineralogic reaction, chilling by either unit up to the contact and including relations are absent. The Wetherstaness ultramafite is cut by granitic pegmatites and aplites of the plutonic complex in numerous places (Figure 3.1-2).

3.1.3.5 Mill Loch ultramafites

Three minor ultramafite masses crop out to the SE of Mill Loch (Figure 3.1-1).

(a) The first is exposed in a 25-30 m long stream section of the E tributary of Mill Burn at GR: [HU 3794 6573] and lies approximately on the pluton-country rock contact. The ultramafite comprises serpentinized peridotite veined by pyroxenite, with steeply dipping, cumulus modal layering trending N-S in places (eg. GR: [HU 3795 6575]).

(b) The second serpentinized ultramafite crops out 120 m E of Mill Loch at GR: [HU 379 660] and is defined on the basis of significant positive magnetic anomaly over the area. The ultramafite, again, lies approximately on the margin of the plutonic complex.

(c) A third ca. 30 m wide, 100 m long ultramafite mass is defined by a series of exposures and a concentration of large ultramafite boulders 50 m E of Mill Loch, GR: [HU 3782 6605]. The ultramafite is elongate N-S, entirely enclosed within the plutonic complex and is spatially associated with mela-gabbronorite and biotite-two-pyroxene diorite. The ultramafite is heterogeneous and is lithologically similar to the Wetherstaness ultramafite (see section 3.1.3.4) and includes: massive websterite, olivine websterite and lherzolite ± biotite ± hornblende; brecciated olivine websterite and lherzolite ± biotite ± hornblende; dunite veined by fine-grained pyroxenite, and dunite.

3.1.3.6 Hill of Burravoe ultramafites

Four separate ultramafite masses crop out in the Hill of Burravoe - Burravoe Burn area (Figure 3.1-1).

(a) Homegeneous, coarse-grained (mean grain size = 2-8 mm), amphibolized pyroxenite and amphibolized hornblende pyroxenite forms a NW-SE trending (strike 138°), ca. 50-70 m wide mass S of Hill of Burravoe, GR: [HU 3668 6760]. The ultramafite mass is sporadically exposed, lies on the margin of the Brae plutonic complex and in places is heavily sheared and altered to secondary tremolite ± cummingtonite ± γ-serpentine ± talc ± carbonate assemblages.

(b) Exposed in the Burravoe Burn stream section at GR: [HU 3674 6723] is a 10 m wide, NW-SE trending (strike 145°) ultramafite dyke, dominantly composed of serpentinized lherzolite and dunite, with minor olivine websterite. Peridotite and pyroxenite lithologies show a grain shape alignment of pyroxene subparallel to the well-defined margins of the dyke. The ultramafite dyke, based on outcrop pattern as actual contacts are not exposed, appears to cross cut the main biotite-two-pyroxene diorite unit of the Brae plutonic complex.

(c) Two small ultramafite masses lie in close proximity to each other SW of Hill of Burravoe at GR: [HU 3647 6737] and GR: [HU 3646 2729]. The outcrops are defined by relatively minor exposures, concentrations of ultramafite boulders and small (<< 20 m across), elliptical, positive magnetic anomalies. The ultramafites lithologically resemble the Wetherstaness ultramafite and comprises websterite, olivine websterite, lherzolite, wehrlite, hornblende-olivine websterite, and brecciated and dunite/wehrlite-veined websterite.

3.1.3.7 Riding Hill ultramafite

An approximately circular sub-drift outcrop of possible serpentinized ultramafite, define purely on the basis of a positive magnetic anomaly, occurs at GR: [HU 387 683]. The ?ultramafite lies within Scatsta quartzitic group rocks. Heavily amphibolized, cumulus phase-layered pyroxenite and serpentinized/steatitized dunite boulders, thought to be derived from the Riding Hill ultramafite, occur at Burn of Valayre, GR: [HU 372 691], 1.5 km NE of Brae village.

3.1.3.8 Brae ultramafites

Two minor ultramafite masses crop out SE of Brae village (Figure 3.1-1) at GR: [HU 3618 6760] ad GR: [HU 3603 6774]. Both masses are poorly exposed, elliptical, elongate N-S and enclosed by biotite-two-pyroxene diorite. The outcrops are defined principally by positive magnetic anomaly systems around the small exposures. The ultramafites comprise of massive olivine websterite and lherzolite (± biotite ± hornblende), with minor, thin (< 50 mm wide) pyroxenite veins. The ultramafites are heavily serpentinized and amphibolized in places.

3.1.4 Contact metamorphism

Contacts of the pluton with country rock are sharp, discordant and characteristically igneous. Contact metamorphic effects related to the emplacement of the Brae plutonic complex occur continuously along country-rock contacts. Granular textures attributed to contact metamorphism locally occur over printing the penetrative gneissose schistosity of the country-rock and extend up to 100 m from the pluton-country rock contact. Contact metamorphic textural changes are accompanied by the development of sillimanite, generally within 100 m of the contact outcrop (Figure 3.1-1). However, in the area between Olna Firth and Loch of Gronfirth, (eg. GR: [HU 38 63]) contact metamorphic sillimanite does occur up to 400 m from the nearest plutonic-country rock contact and may indicate the plutonic complex lies at shallow depth beneath the area. The sillimanite statically overprints earlier regional metamorphic, kyanite-grade amphibolite-facies assemblages.

Probably the most interesting contact metamorphic effects are shown by rocks in the inner aureole or in xenoliths within the plutonic complex.

In close proximity to some pluton-country rock contacts veins of granitic material are developed and are interpretated to be locally derived during incipient anatexis of the country rock.

At one locality within the Wetherstaness ultramafite, exposed in the cliff section W of Wetherstaness, GR: [HU 3571 6511] is a leucocratic, elliptical xenolith approximately 10 m across enclosed in partially serpentinized olivine websterite.

The central portion of the xenolith is white and comprises homogeneous, medium-grained, anhedral-granular textured clinopyroxenite. The margins of the xenolith are pale-green and comprise of a homogeneous, anhedral-granular textured, clinopyroxene-tremolite-serpentine assemblage. Mineralogically, the central clinopyroxenite portion consists wholly of Cr-poor diopsidic clinopyroxene (Wo 51.1:En 44.7:Fs 4.2; 100Mg/(Mg + Fe) = 91.3; Al_2O_3 = 5.72%; Cr = 50 ppm; Sr = 100 ppm) and shows fine-scale, (100) orthopyroxene exsolution lamallae. It is clear from the textural and mineralogical evidence that the clinopyroxenite probably represents an included and contact metamorphosed siliceous dolomitic limestone xenolith and is not part of the plutonic igneous lineage.

In the marginal-facies diorite units of plutonic complex xenoliths are abundant and are characteristically rather nebulous and completely recrystallized (eg. Figure 3.1-5a and b). Two-pyroxene granulites are a common xenolith species in these units. Whole-rock major and trace element geochemical, textural and mineralogical data distinguish these rocks from those of the plutonic complex proper (cf. Gill, 1965). Mineralogically, the two-pyroxene granulites consist essentially of Cr-poor salite clinopyroxene (Wo 45.0:En 35.0:Fs 20.0; 100Mg/(Mg + Fe) = 63.5; Al_2O_3 = 3.39%; Cr = 100 ppm), hypersthene/ferro-hypersthene (En = 50.5; Al_2O_3 = 1.98; Ni = 70 ppm) and labradorite plagioclase.

To the SE of Wetherstaness, near Pinchdyke, GR: [HU 3597 6481], an elongate mass of country-rock amphibolite gneiss is exposed along the shore section (Figure 3.1-2). The amphibolite gneiss is disrupted by extensive late faulting (which also affects plutonic complex rocks in the area) and is in contact with marginal-facies diorite/gabbronorite unit rocks. The central portion of the mass has a well-developed, blastomylonitic, gneissose foliation, with plagioclase-rich and hornblende-rich lenticular domains (Figure 3.1-5c). At the W margin of the mass, the amphibolite gneiss is hornfelsed and develops an unusual contact metamorphic assemblage. In this contact zone plagioclase-rich domains of the amphibolite gneiss are replaced by a granular plagioclase-biotite assemblage and the hornblende-rich domains by an unusual garnet-orthopyroxene-green spinel (hercynite)-Fe-Ti oxide assemblage (Figure 3.1-6a). Texturally, the hornfels shows no preferred orientation of grains, garnet is invariably surrounded by a corona of orthopyroxene, with spinel and Fe-Ti oxide partially enclosing both these minerals (Figure 3.1-6b). Mineralogically, the plagioclase is labradorite (An = 57.7 - 61.4), the biotite is a phlogopitic biotite (100 Mg/(Mg + Fe) = 61.5 - 62.7; SiO_2 (hydrous) = 36.1 - 36.5%; TiO_2 (hydrous) = 1.78 - 2.33%), the orthopyroxene is hypersthene (En = 57.5 - 59.6; Al_2O_3 = 4.98 - 6.3%), the garnet is almandine-rich (Al_2O_3 = 21.55 -22.17%; MgO = 8.05 - 8.65%; CaO = 2.22 - 2.81%; FeO* = 24.62 - 25.01%), the green spinel is hercynitic (Al_2O_3 = 57.06 - 58.46%; FeO* = 31.63 - 34.05%; MgO = 7.65 - 7.93%), and the Fe-Ti oxide is ilmenite.

The inner-contact zone and xenolith mineralogies are indicative of pyroxene hornfels-facies contact metamorphic conditions. The predominance of hornfels textures and the preservation/non-disruption of the earlier regional gneissose foliation into the contact aureole suggests that pluton emplacement was essentially decoupled from the country rock and non-tectonic.

3.1.5 Petrography and mineralogy

3.1.5.1 Ultramafite units

The ultramafic rock types strictly include: websterite, olivine websterite, lherzolite, wehrlite, olivine clinopyroxenite and dunite, ± biotite ± brown hornblende ± chrome-spinel ± Fe-Ti oxide ± apatite. Olivine and orthopyroxene are frequently serpentinized; orthopyroxene and Ca-rich clinopyroxene may be amphibolized to colourless clinoamphibole. All ultramafites have Ca-rich clinopyroxene > orthopyroxene and plagioclase is completely absent. The ultramafites are typically medium- to coarse-grained (mean grain size = 1 - 5 mm), equigranular, euhedral- to anhedral-granular textured (Figure 3.1-4c and e, and Figure 3.1-5d) adcumulates or mesocumulates. The adcumulates have no recognisable, discrete, postcumulus material and mutual interference grain boundaries of unzoned cumulus grains are common. The mesocumulates frequently comprise about 10-20% by volume postcumulus material, either as a zoned overgrowth on cumulus grains or as intercumulus grains, usually biotite or brown hornblende. A grain shape fabric (igneous lamination) is apparent in some peridotites and pyroxenites both in hand specimen and thin section, where the long dimensions of subhedral pyroxenes have a subparallel arrangement. Microrhythmic (< 10 cm thick), phase and modal layering is occasionally seen in some ultramafites. Layers are laterally and stratigraphically discontinuous, layer contacts are generally sharp and concordant.

Ca-rich clinopyroxene is enhedral to anhedral, equant to tabular, medium- to coarse-grained (mean grain size = 1-5 mm) show mutual interference grain boundaries with olivine and orthopyroxene, may be zoned or unzoned and exsolution lamallae parallel to (100) are commonly seen (eg. Figure 3.1-4c). In some sections clinopyroxene neoblasts lie along original grain boundaries suggesting partial recrystallization. The Ca-rich clinopyroxene is a low-Al, chrome-diopside (Wo 44.2 - 45.5:En 45.4 - 47.5:Fs 8.2 -9.9; Mg/(Mg + Fe) = 82.0 - 86.8; Al_2O_3 = 2.23 - 3.36%; TiO_2 = 0.30 - 0.60%; Na_2O = 0.1 - 0.47%; Cr = 700 - 2700 ppm), with a small compositional range within any thin section and a slight Fe enrichment trend in the ultramafites as a whole. The Cr content of the Ca-rich clinopyroxene is quite variable, but generally high, which reflects the partitioning of Cr into early formed Mg-rich clinopyroxenes.

Orthopyroxene is petrographically similar to the Ca-rich clinopyroxene (Figure 3.1-4e) and is bronzite (Wo 1.2 - 2.6:En 78.7 - 81.3: Fs 16.9 - 19.2; Mg/(Mg + Fe) = 80.4 - 82.6; Al_2O_3 = 2.15 - 2.93%; TiO_2 = 0.11 - 2.93%).

The olivine is subhedral-anhedral, equant, medium-grained (mean grain size = 1 - 2 mm), has mutual interference grain boundaries with pyroxene (Figure 3.1-4e) or is intergranular to well formed pyroxene grains and is forsteritic (Fo = 78.7 - 81.6; NiO = 0.07 - 0.23%; CaO = 0.02 - 0.14%).

Accessory brown hornblende in the ultramafite occurs as anhedral, medium- to coarse-grained (mean grain size = 1-5 mm) oikocrysts enclosing chadacrysts of orthopyroxene (Figure 3.14b) and/or olivine, or replacing and/or rimming earlier clinopyroxene, or as a late, intercumulus phase. The hornblendes show a wide compositional range, from edenitic hornblende to pargasite (nomenclature of Leake, 1978). Decreasing Mg/(Mg + Fe^{2+}) in the hornblende is accompanied by increasing SiO_2, Al_2O_3, TiO_2, K_2O and decreasing Cr_2O_3 (Mg/(Mg + Fe) = 75.7 - 85.9; SiO_2 = 43.07 - 48.16%; Al_2O_3 = 9.47 - 13.24%; TiO_2 = 1.12 - 1.91%; Na_2O = 1.96 - 21.5%; K_2O = 0.11 - 1.19%; Cr_2O_3 = 0.68 - 1.1% (all % on a hydrous basis). Accessory biotite forms small anhedral, interstitial (intercumulus) grains and is a Ti-rich phlogopite. Primary oxides range from chrome-spinel to ilmenite and form small, accessory, anhedral to subhedral grains.

Olivine in most peridotites, pyroxenites and dunites is partially replaced by pseudomorphic, mesh-textured α-serpentine (probably lizardite), with magnetite concentrations along the cords (Figure 3.1-4e). Close study of the pseudomorphing textures and relic olivine cores in optical continuity define the original grain boundaries. Orthopyroxene is occassionally replaced by Mg-cummingtonite either as a partial or complete mantle around pyroxene, as well as by aggregates of cummingtonite blades with little or no relic orthopyroxene remaining. Ca-rich clinopyroxene may be partially or wholly replaced by tremolite. Non-pseudomorphic, interpenetrative and ribbon-textured γ- or α-serpentine dominated secondary assemblages, along with steatites, are found in locally developed, discrete shear zones throughout the ultramafite units.

Brecciated ultramafites have a widespread distribution within the different ultramafite masses of the plutonic complex. Anastomosing dunite and wehrlite veins and dykes disrupt massive pyroxenite and peridotite (see section 3.1.3.4). The dunite and wehrlite veins are generally fine-grained (mean grain size = 0.05 - 0.4 mm), equant, anhedral-granular textured, with olivine and opaque oxide (?magnetite) uniformally distributed. On a fine scale dunite veins are seen to penetrate along host rock pyroxene grain boundaries (Figure 3.1-4d) and disrupt the rock peridotite or pyroxenite.

3.1.5.2 Cu-Ni-Fe sulphide-bearing ultramafites

Cu-Ni-Fe sulphide-bearing websterite and olivine websterite form the Wetherstaness ultramafite (see section 3.1.3.4) are fine- to medium-grained (mean grain size = 0.2-1 mm), with an equigranular, subhedral-granular (with mutual interference grain boundaries) (Figure 3.1-6d) to inequigranular, poikilitic texture (Figure 3.1-6c). Where the sulphide-ore occurs as oikocrysts enclosing pyroxene or olivine there is an increase in silicate grain-size, via a transitional margin, into the surrounding 'host' ultramafite (Figure 3.1-6c and d). The tendency for increased olivine and pyroxene grain size outside the sulphide-bearing areas suggests silicate growth may have been effectively arrested within the sulphide-rich areas. In places the sulphide-rich areas are continuous across silicate phase and modal cumulate layering (Figure 3.1-6e).

Olivine in the sulphide-bearing ultramafites is equant, subhedral, fine- to medium-grained (mean grain size = 0.2-1 mm), with variable alteration to pseudomorphic, mesh α-serpentine and magnetite, and forsteritic (Fo = 78.9). Olivine is a minor mineral phase in most sulphide-bearing ultramafites and has mutual interference grain boundaries with pyroxene and sulphide-ore minerals. Ca-rich clinopyroxene and orthopyroxene occur as equant, subhedral, fine- to medium-grained (mean grain size = 0.2-1 mm), granular grains. The Ca-rich clinopyroxene shows a pronounced (100) unmixing texture, with ilmenite on the (100) parting giving a dark body colour (Figure 3.1-6c) and is chrome-diopside (Wo 45.2:En 47.5:Fs 7.3; 100 Mg/(Mg + Fe) = 86.8; Al_2O_3 = 2.23%; Cr = 1250 ppm). Orthopyroxene also carries a fine, lamellar and blebby (cpx-daughter) exsolution parallel to (100) and is bronzite (En = 79.0; Al_2O_3 = 2.29%; CaO = 1.35% Ni = 140 ppm). Both orthopyroxene and Ca-rich clinopyroxene are mostly unzoned. Although in some rocks grains are zoned, with a noticable absence of exsolution lamallae at the margins (Figure 3.1-6c).

Sulphide-ore mineral phases do not replace silicate phases and are not related to areas of secondary alteration. The sulphide-ore generally occurs as separate, anhedral, equant, granular or poikilitic grains of the main mineral types. Pyrrohotite, the most abundant sulphide, is optically homogeneous or shows a flame exsolution of ?troilite and lamallar exsolution of pentlandite. Separate grains of pentlandite (NiO = 25-35%; CoO ≈30%), with characteristic triangular cleavage pits, are optically homogeneous.

Chalcopyrite occurs as rare, separate, small grains with variably developed lamallar twinning and fine-scale, exsolved lamallae of ?mackinawite of probable high temperature origin.

3.1.5.3 Other lithological units

(a) Gabbronorites form a minor part of the Brae plutonic complex and are restricted to the marginal-facies, two-pyroxene diorite/gabbronorite units. Rock types include, gabbronorite (orthopyroxene gabbro), hornblende gabbronorite, biotite-hornblende gabbronorite and amphibolized gabbronorite. Contacts between two-pyroxene diorite and gabbronorite are occassionally sharp, but most are gradational over a few meters. The gabbronorites are typically medium-grained (mean grain-size ≈ 1 mm), homogeneous, equigranular and range from anhedral- to subhedral-granular. Mineralogically, the gabbronorites consist of plagioclase (labradorite) - Ca-rich clinopyroxene - orthopyroxene - Fe-Ti oxide ± brown hornblende ± biotite ± apatite. Clinopyroxene and orthopyroxene make up 30-40% of the rock. Hornblende partially replaces clinopyroxene, generally only in traces, but locally it forms as much as 15% of the rock. Clinopyroxenes and orthopyroxenes form a compositional continuum with those in the ultramafites; the clinopyroxene is a low-Al, high-Cr augite or salite (Wo 40.6 - 45.1:En 40.9 - 48.7:Fs 10.7 - 15.4; Mg/(Mg + Fe) = 78.9 - 81.4; Al_2O_3 = 2.31 - 4.27%; TiO_2 = 0.42 - 0.73%; Cr = 850 - 1800 ppm) and the orthopyroxene is bronzite or hypersthene (En = 59.0 - 77.1; Al_2O_3 = 1.93 - 3.09%; Ni = 100 - 550ppm). The minor brown hornblende (Mg/(Mg + Fe) = 64.7 - 75.1; SiO_2 = 45.87 - 46.16%; Al_2O_3 = 10.41 - 11.16%; TiO_2 = 1.68 - 2.01%; Na_2O = 1.37 - 1.42%; K_2O = 0.42 - 0.87%; Cr =

800 - 1400 ppm; all % on a hydrous basis) varies compositionally from edenite to edenitic hornblende (nomenclature after Leake, 1978). Secondary minerals include tremolite and Mg-cummingtonite replacing pyroxene.

(b) The two-pyroxene diorites are heteregeneous and consist mainly of biotite-two-pyroxene diorite, hornblende-biotite-two-pyroxene diorite, biotite-magnetite-two pyroxene diorite and amphibolized biotite-two-pyroxene diorite. The lithologies are typically fine- to medium-grained (mean grain-size = 0.3 - 2 mm) and have homogeneous or heterogeneous, subhedral- to anhedral-granular textures. An igneous lamination occurs in some units. The two-pyroxene diorites are primarily composed of 50-70% subhedral, slightly zoned plagioclase (andesine) crystals and lesser amounts of granular Ca-rich clinopyroxene, orthopyroxene and Fe-Ti oxides. Biotite (reddish brown), hornblende (green or green-brown), orthoclase (microperthitic) and quartz are present in minor trace amounts. Apatite, sphere, zircon, rutile and epidote are seen in some rocks. Late-stage amphibolization occurs on a variety of scales, from small patches in individual sections to large areas of the central portion of the plutonic complex, eg. around Burravoe and Sparl (Figure 3.1-1). Mineral compositional trends within the two-pyroxene diorites are continuous with those of the gabbronorites and ultramafites. The Ca-rich clinpyroxene is augite or chrome-augite (Wo 40.4 - 43.4:En 40.2 - 47.2:Fs 9.9 - 16.8; Mg/(Mg + Fe) = 70.5 - 82.5; Al_2O_3 = 2.36 - 3.09%; TiO_2 = 0.35 - 0.78%; Na_2O = 0.41 - 0.68%; Cr = 700 - 2700 ppm). Orthopyroxene ranges between bronzite and hypersthene (Wo 28.8 - 39.6:En 57.7 - 76.5:Fs 2.5 - 3.6) and the primary hornblende is an edenitic-hornblende (nomenclature after Leake 1978) (eg. Mg/(Mg + Fe) = 73.9; SiO_2 = 46.87%; Al_2O_3 = 10.21%; TiO_2 = 2.01%; Na_2O = 1.2%; K_2O = 0.68%; Cr = 1400 ppm; all % on a hydrous basis).

(c) Hornblendites, hornblende gabbros and hornblende diorites form a heterogeneous suite, with grain sizes as variable as the mode, and occur as a series of stock-like, satellite intrusion S of Olna Firth and minor masses within the main Brae outcrop. Age relations between these hornblendic lithologies are complex with gradational contacts and multi-brecciation common. The hornblendic rocks are typically medium- to coarse-grained (mean grain size = 1 - 10 mm), equigranular and have enhedral- to subhedral-granular textures. An igneous lamination, with subparallel alignment of tabular hornblende and plagioclase, and cumulus modal layering are obvious in some rocks. The hornblendic rocks are primarily composed of tabular, enhedral to subhedral, zoned, intermediate to calcic plagioclase and green-brown hornblende. Fe-Ti oxide and apatite are ubiquitous accessories. Modal biotite, quartz and orthoclase are present in dioritic units. Relic pyroxene is occassionally seen in the cores of some hornblendes and indicate a possible petrgraphic link with the two-pyroxene rocks. Hornblendes are frequently rhythmically zoned with generally brown (?high T) cones in optical continuity with green-blue (?low T) rims and are edenitic-hornblende (nomenclature after Leake, 1978) (eg. Mg/(Mg + Fe) = 58.9 - 65.9; SiO_2 = 44.37 - 46.91%; Al_2O_3 = 10.57 - 7.96%; TiO_2 = 0.9 - 0.81%; Na_2O = 1.15 - 1.21%; K_2O = 0.36 - 0.78%; Cr = 450 - 320 ppm; all % on a hydrous basis).

(d) Granitic leucocratic rocks occur as late-intrusive bodies and comprise <10% of the plutonic complex. Biotite granodiorite and tonalite are the most common rock types, with minor amounts of biotite-hornblende tonalite, rare, two-mica tonalite and biotite granite. The granitic leucocratic rocks are generally medium-grained (mean grain-size = 1 - 5 mm), equigranular or porphyritic, subhedral- to anhedral-granular and characterized by abundant quartz, plagioclase (oligoclase) and a low mafic mineral content ± Microcline or orthoclase ± apatite ± zircon ± Fe-Ti oxide. Aplites (quartz-microcline-oligoclase) and granitic pegmatites are common throughout the plutonic complex.

3.1.6 Major and trace element geochemistry

Major and trace element data from rocks of the Brae plutonic complex are present in Table 3.1-2 and Gill (1965). Whole rock major element data shows a wide and near continuous variation for the analysed rock units. The evolutionary 'series' is, however, a complex one and should be viewed in the light that it contains a combination of rocks, some possibly near melt composition and others formed by successive accumulations of crystals from a magma body undergoing fractional crystallization.

3.1.6.1 AFM diagram

In the AFM diagram (Figure 3.1-8), Brae plutonic complex rocks form a typical calc-alkaline trend (cf. Lopez-Escobar et al., 1979), stretching from the AF side to the FM side of the diagram. The calc-alkaline AFM trend is, on one level, dominantly a product of the varying modal abundance of the main mineral phases: olivine, Ca-poor pyroxene, Ca-rich pyroxene, hornblende, biotite, feldspar and quartz. The trend is not continuous, with an obvious gap separating the diorites from the felsic differentiates and hybridized diorites. This gap corresponds to the incoming of alkali feldspar and more-sodic plagioclase as modally significant mineral phases in these leucocratic plutonic rocks. It is also perhaps important to note that some of the plutonic gabbros and diorites have relatively high total Fe contents. This limited Fe-enrichment is manifested in the composition of the mafic mineral phases (eg. Fe-rich hyperthene). The initial FM side of the AFM trend resembles the Fe-enrichment of crystal fractionated tholeiitic bodies.

3.1.6.2 Ultramafite units

Whole-rock major and trace element data for the ultramafites is given in Table 3.1-2 and Gill (1965) and is plotted against the fractionation index 100 Mg/(Mg + Fe^{2+}) in Figure 3.1-9, 10 and 11. The fractionation index (100 Mg/(Mg + Fe^{2+}) ratio or Mg′-value) is used to the investigation of possible crystal-liquid fractionation processes and varies between 0 and 100. The Mg′-value is essentially unaffected by the crystallization of plagioclase. It is particularly useful in the study of olivine-pyroxene-plagioclase cumulates in which mineral compositions are approximately the same (and which therefore are assumed to have crystallized from virtually identical parental melts). Here Mg′-values, irrespective of the proportions of minerals present, will be almost identical because of the closely similar Mg/Fe ratios of coexisting mafic mineral phases. It is this attribute which dictates that both peridotites and pyroxenites from the Brae plutonic complex have similar high Mg′-values (83.8 - 91.4). Major element variation within the ultramafites tends to reflect differences in modal mineral content, with an overall trend from Mg-rich (dunite) to more Ca-rich (pyroxenite). Peridotites show higher MgO and lower CaO, SiO_2, Al_2O_3 and Na_2O_3 compared with the pyroxenites.

Compatible trace element abundances in the ultramafites show a wide variation (eg. Ni = 370 - 3513 ppm; Cr = 1350 - 3307 ppm; Co = 68 - 133 ppm). Variation in compatible trace elements show a good correlation with modal olivine, pyroxene and chrome-spinel. Sc values (1 - 51 ppm) also vary directly with the modal mineral content of the ultramafites, with peridotites showing consistently lower Sc than the pyroxenites. This feature is consistent with the fact that Sc is incompatible with olivine and compatible with pyroxene, particularly Ca-rich clinopyroxene.

All ultramafites from the Brae plutonic complex show low abundances of incompatible trace elements (eg. Y = 3 - 12 ppm; TiO_2 = 0.01 - 0.72%; Zr = 3 - 50 ppm; Sr = 1 - 78 ppm) and are mainly lower than the gabbro-diorite-granite units of the complex. The incompatible trace element V is a notable exception, two pyroxenite samples show V abundances of about 200 ppm, probably reflecting the significant modal Fe-Ti oxide content of these ultramafites. The otherwise low incompatible trace element abundances indicate the almost complete partitioning of these elements into the coexisting melt and tend to support the interpretation of the ultramafites as adcumulates or mesocumulates. Variation in incompatible trace elements appears to be partly related to modal mineralogy, including the amount of postcumulus material. For example, clinopyroxene-rich, biotite- or amphibole-bearing ultramafites have consistently higher Ti, Zr and Sr values than the olivine-rich ultramafites. These elements also show a slight negative correlation with the Mg′-value fractionation index. This is consistent with the clinopyroxene-rich, biotite- or amphible-bearing ultramafites being derived from more-evolved parental magma(s) and/or they contain a greater proportion of postcumulus material.

3.1.6.3 Other lithological units

Whole-rock major and trace element data for the *gabbro*-diorite-granite units is given in Gill (1965) and is plotted against the fractionation index 100 $Mg/(Mg + Fe^{2+})$ *in Figure* 3.1-9, 10 and 11.

Despite significant dissimilarities in mineralogy, the gabbronorite and two-pyroxene diorite units, and the hornblende gabbro and hornblende diorite units show no meaningful major element geochemical differences at comparable stages of fractionation.

All major elements show mean continuous variation with the Mg′-value fractionation index. Mg′-values show a positive correlation with MgO and CaO and a negative correlation with SiO_2, Al_2O_3 and Na_2O. The decrease in MgO with decreasing Mg′-value probably reflects mafic-mineral fractional crystallization controlled evolution of the more-fractionated melts. A similar decrease in CaO with fractionation is consistent with Ca-rich clinopyroxene, and/or hornblende and/or plagioclase fractional crystallization. However, a steady increase in Al_2O_3 with fractionation in the gabbros and diorites tends to preclude significant amounts of plagioclase fractional crystallization during their evolution. In the more-evolved leucocratic units of the plutonic complex Al_2O_3 and Na_2O show a slight decrease with Mg´-value, consistent with sodic plagioclase controlled fractional crystallization.

Compatible trace element abundances in the gabbros, diorites and granitic leucocratic units are variable (eg. Ni = 3 - 320 ppm; Cr = 12 - 900 pm; Co = 18 - 70 ppm), generally low and show a positive correlation with Mg´-values. The variation trends form a continuation of the trends defined by the ultramafites and are consistent with mafic-mineral controlled fractional crystallization (probably involving pyroxene and/or hornblende, rather than olivine) during gabbro-diorite evolution.

The incompatible trace elements (eg. V, Y, Ti, Zr and Sr) show a general negative correlation with the Mg´-value fractionation index for the gabbros and diorites. These features are, again, consistent with magmatic differentiation controlled by mafic-mineral fractional crystallization. The overall increase in Sr with fractionation is, however, hard to reconcile with significant plagioclase fractional crystallization in the plutonic system. The general decrease in Ti and V with increase fractionation in the more-evolved leucocratic units suggests tha amphibole and/or small quantities of Fe-Ti oxides may have been fractionating phases. A similar poorly defined decrease in Zr and Y in the same rocks may point to minor, zircon fractional crystallization.

3.1.7 Rare earth element geochemistry

The biotite-olivine websterite BB212 (64125) is characterized by low total rare earth element (REE) abundances (Table 3.1-3). The chondrite-normalized REE profile displays a moderate LREE enrichment (Ce_N/Yb_N = 6.74) relative to HREE (Figure 3.1-12). Another noteworthy feature of the REE profile is a small negative Eu anomaly which may be probably due to the fractionation of plagioclase in the parental magma, with the preferential stabilization of Eu^{2+} reflecting the prevailing oxygen fugacities, melt composition and structure (Moller and Muecke, 1984). Similar REE characteristics have been recorded from ultramafic lithologies from the Bear Mountain igneous complex (Snoke et al., 1981), as shown in Figure 3.1-12. Ultramafic lithologies from many layered intrusive complexes also show similar moderately fractionated chondrite-normalized patterns (see section 4.1).

The cumulus nature of the biotite-olivine websterite means that the REE content of the rock depends essentially on two factors: (a) the composition of the parental melt, and (b) the relative proportions of cumulus minerals and postcumulus material. The ultramafite is a mesocumulate/adcumulate, therefore, given that the mineral constituents of the rock have REE partition coefficients less than 1, and clinopyroxene and biotite (the main REE bearing phases) would be expected to partition the HREE, relative to the LREE (cf. Arth and Hanson, 1975; Frey et al., 1978; Henderson, 1984), a qualitative model of the REE character of the parental magma can be achieved. Under these considerations, the LREE-enriched and high total REE character of the biotite-olivine websterite suggests it accumulated from a LREE-enriched, high REE (?primitive) parental magma, even allowing for a significant postcumulus component (which arose from the closed system crystallization of trapped residual parental magma) in the rock.

3.1.8 Petrogenesis

3.1.8.1 Ultramafite units

Textural features, lack of mineral zoning, rare cumulus layering, and high compatible element and low incompatible element abundances of the Brae plutonic complex ultramafites support the hypothesis that *many of the ultramafites represent* crystal cumulates. The predominance of probable adcumulates over mesocumulates is indicative of relatively open-system magmatic crystallization conditions. Internal structural relations suggest the ultramafites pre-date or are contemporaneous with the main two-pyroxene diorite units. The lack of contact metamorphic or hybridization features with the enclosing two-pyroxene diorite units probably indicates the ultramafites were introduced into the present level within the complex as crystalline or partially crystalline 'cool' masses. Ultramafite dykes, at Gronfirth Runie (see section 3.1.3.1) and Hill of Burravoe (see section 3.1.3.6), show an igneous lamination parallel to the margins and are supportive of an emplacement origin as partially crystalline magma masses.

If the ultramafites represent early formed cumulates, identification of the primitive parental magma(s) from which the ultramafites crystallized may provide an important constraint on possible unfractionated, mantle-derived, primary magma(s) in such plutonic systems. The lack of any obvious candidates for such primitive parental magma(s) within the plutonic suite represents a significant stumbling block when attempting to model the petrogenesis of the ultramafites. Nevertheless, the following petrological constraints on the nature of the primitive parental magma(s) to the ultramafites can be imposed from the data.

(a) The ultramafites, with olivine (Fo $\leq$ 81.6), bronzite (Mg/(Mg + Fe) $\leq$ 82.6), chrome-diopside (Mg/(Mg + Fe) $\leq$ 86.8) and magnesian Cr-rich amphibole (Mg/(Mg + Fe) $\leq$ 85.9), have moderate Mg/Fe ratio equilibrium primitive parental magma(s) (magma Mg′-value $\leq$ 55.8 (53.2 - 58.1), using ol-melt K_D of 0.30 ± 0.03 (Roder and Emslie, 1970; magma Mg′-value $\leq$ 60.2 (58.0 - 62.1), using cpx-melt K_D of 0.23 ± 0.02 (Grove and Bryan, 1983).

(b) The high compatible trace element abundances in cumulus olivine (Ni $\leq$ 1807 ppm), and chrome-diopside (Cr $\leq$ 2700 ppm) are consistent with basic or possibly ultrabasic melts being parental to the ultramafites (magma Cr = 270 ppm, using the cpx-melt K_D of 10; magma Ni = 150 ppm, using the ol-melt K_D of 12 (Sun et al., 1979)].

(c) Both the moderate Mg/Fe ratio and moderate compatible trace element character of the equilibrium primitive parental magma(s) do not support the idea that the ultramafite are the first crystallization products of primary mantle-derived melts.

(d) The predominance of pyroxene, rather than olivine, in the ultramafites suggests moderate silica activity in the parental magma(s).

(e) Ca-rich clinopyroxene ± olivine ± orthopyroxene ± chrome-spinel ± Fe-Ti oxide are probable liquidus mineral phases for the primitive parental magma(s). The relative abundance of dunite and clinopyroxene-rich ultramafite suggests that a lesser period of olivine crystallization was accompanied by extensive, possibly cotectic, clinopyroxene-dominated crystallization.

(f) Accessory biotite and hornblende are late magmatic and/or replacive in the ultramafites and represent crystallization of a hydrous intercumulus silicate melt enriched in alumina and alkalies, and not primary cumulus crystallization. Hornblende is not a near liquidus phase and therefore the upper thermal stability limited of amphibole cannot be used to estimate the liquidus temperature of the parental magma(s).

(g) The widespread occurrence of accessory biotite and hornblende in the ultramafites suggest the parental magma(s) were hydrous, but vapour-undersaturated. Accessory biotite may suggest a mild alkaline affinity to the parental magma(s).

(h) High REE abundances relative to chondrite and overall LREE-enriched profile of a Ca-clinopyroxene- and olivine-dominated accumulative ultramafite (see section 3.1.7) suggest a parental magma enriched in LREE compared to most mid-ocean ridge basalts and island arc tholeiites (cf. BVSP, 1981, Saunders, 1984).

Whole-rock major and trace element variations in the ultramafites are dominantly controlled by modal mineralogy, with incompatible trace element abundances possibly reflecting amounts of post-cumulus material. Geochemical variations due to differences in parental magma composition cannot be definitely resolved from the whole rock analytical data.

Anastomosing dunite and wehrlite dyke-vein systems cross-cutting massive pyroxenite or peridotite occur throughout the Brae plutonic complex (see section 3.1.3). Similar features are found in Alaskan-type complexes (Irvine, 1963, 1974), Alpine-type complexes (Dick, 1977; Dungan and Ave-Lallement, 1977; Quick, 1981), Layered complexes (Cameron and Desborough, 1964; Schiffries, 1982; Raedeke and McCallum, 1984), and Appinite-type complexes (James, 1971; Kelemen and Ghiorso, 1986). A variety of origins have been proposed for the anastomosing dunite and wehrlite dyke-vein systems and include: (a) partial melting of the host ultramafite, leaving an olivine-rich restite (Boudier and Nicolas, 1972; Dick, 1977; Jackson and Ohnenstetter, 1981; Nicolas and Jackson, 1982); (b) incongruent dissolution of pyroxene by an H_2O-rich magma or fluid phase (infiltration metasomatism) (Cameron and Desborough, 1964; James, 1971; Dungan and Ave-Lallement, 1977; Irvine, 1974, 1980; Raedeke and McCallum, 1984), and (c) olivine ± Ca-rich clinopyroxene accumulation from a high magnesian magma in the dyke-vein systems (Quick, 1981). Field and petrographical features in the Brae plutonic complex tend to preclude a partial melting origin, especially as the refractory vein material appears to be secondary and the host pyroxenites and peridotites primary.

Petrographical features suggesting transformaion of pyroxene to olivine on any scale are absent. Therefore, it seems probable that the anastomosing dunite and wehrlite dyke-vein systems are accumulative in origin; the increased grain size of Ca-rich clinopyroxene in the veins possibly reflecting renewed crystal growth from the intruding melt.

Petrographical and mineralogical features of the Cu-Ni-Fe suphide-bearing ultramafites (see section 3.1.5.2) indicate sulphide crystallization was penecontemporaneous with that of pyroxene and olivine in the cumulate. Similar poikilitic 'net-textured' sulphide mineralization has been described from some komatiite units (eg. Naldrett and Campbell, 1982) and is regarded as primary magmatic in origin. The low solubility of S in basic melts and lower crystallization temperatures of the sulphides allows the generation of immiscible sulphide liquids in many basaltic systems (cf. BVSP, 1981). It is proposed that the Cu-Ni-Fe sulphide-bearing areas of ultramafite within the Brae plutonic complex formed by the amalgamation of immiscible sulphide droplets as crystallization of silicate phases proceeded. Decreasing temperature and activity of FeO, the later by crystallization of Fe-bearing oxides and silicates, inducing separation and/or exsolution of the immiscible sulphide phase from the basic/ultrabasic silicate melt. Possible remobil-ization of the pyroxene-olivine cumulus framework and/or final crystallization of the cumulate prevented complete mobilization and removal of the dense immiscible sulphide melt phase.

3.1.8.2 Other lithological units

The ultramafite units appear to be petrologically related (comagmatic) to the two-pyroxene diorites and gabbronorites. The critical observations in support of this conclusion are:

(a) the similarities in modal mineral phases (Ca-rich clinopyroxene ± orthopyroxene ± brown hornblende ± biotite) between the ultramafites and the gabbronorites and two-pyroxene diorites;

(b) the similar characteristics in Ca-rich clinopyroxene from the ultramafite to the gabbronorites and two-pyroxene diorite rocks (ie. Ca-rich, low Al_2O_3 and progressive Fe enrichment);

(c) the near continuous trends on 100 $Mg/(Mg + Fe^{2+})$ variation diagrams, mineral compositions, and the AFM diagram, which shows a characteristic calc-alkaline magmatic evolutionary trend.

The data are consistent with the two-pyroxene diorites and gabbronorites being derived by fractional crystallization from magma residual to or more evolved from the primitive parental magma to the accumulative ultramafites.

The two-pyroxene rocks did not crystallize under conditions of high PH_2O as indicated by the predominance of early crystallizing anhydrous minerals, the low Al-clinopyroxene and moderate Fe enrichment. However, the ignorance of the pigeonite inversion field in the Ca-poor pyroxenes probably reflects a depression of the pyroxene liquidus to a temperature below the pigeonite-orthopyroxene inversion with moderate pH_2O conditions.

The decrease in major elements MgO, CaO, and compatible trace elements Ni, Cr, Co with increasing differentiation (decreasing Mg′-value), coupled with increased Al_2O_3 and incompatible trace elements V, Y, Ti, Zr, Sr is consistent with mafic-mineral controlled fractional crystallization within the two-pyroxene rocks. The crystallizing phases, probably include Ca-rich clinopyroxene ± olivine ± orthopyroxene, the main cumulus mineral phases in the ultramafites. If the gabbronorites and two-pyroxene diorites are regarded as non-cumulus, plagioclase is effectively excluded as a significant cumulus phase by the steady increase in Al_2O_3 and Sr with differentiation. The gradually diminishing Ni abundances in the two-pyroxene rocks precludes extensive olivine fractionation.

Hornblendites, hornblende gabbros and hornblende diorites have a complex multi-intrusion history which hinders detailed analysis of their petrogenesis. However, petrographic and structural features suggest that they are contemporaneous or younger than the two-pyroxene diorite units. Major and trace element similarities with the two-pyroxene rocks at comparable stages of differentiation are consistent with a similar parental magma composition. However, the presence of hornblende as a possible liquidus or near liquidus phase in some rocks indicates the probable high pH_2O of the parent magma(s).

Granitic leucocratic rocks of the plutonic complex show a continuous variation in petrographical, mineralogical and geochemical features from more-evolved members of the diorite units. The geochemical data are consistent with these felsic differentiates being evolved by fractional crystallization from a 'dioritic' parental magma, though a partial melting origin cannot be discounted. Differentiation within the granitic leucocratic rocks, with a noticeable decrease in Al_2O_3 and Na_2O, Ti and V, Zr and Y, appears to be controlled by Na-rich plagioclse, amphibole and/or minor Fe-Ti oxide, and possible zircon fractional crystallization. Late K-feldspar replacement, characteristic of some granite leucocratic rocks, implies an alkali-rich fluid developed during late magmatic stages.

3.1.9 Summary and conclusions

(a) Ultramafites within the Brae plutonic complex comprises a heterogeneous peridotite, pyroxenite and dunite lithological assemblage. Rock types contain combinations of chrome-diopside ± olivine ± bronzite ± biotite ± brown hornblende ± chrome spinel ± Fe-Ti oxide ± apatite (chrome-diopside > bronzite). Cumulus petrographical and rare layering features coupled with the high compatible/low incompatible element abundances in the ultramafites identifies them as probable adcumulates and mesocumulates. The ultramafites pre-date or are broadly contemporaneous with the two-pyroxene diorite and gabbronorite units within the plutonic complex and appear to have been emplaced as crystalline or partially crystalline masses. Patches of Cu-Ni-Fe sulphide in some ultramafites are regarded as the crystallization product of an aggregated immiscible sulphide melt. Anastomosing dunite and wehrlite dyke-vein systems cross-cutting massive ultramafite possibly represent incongruent dissolution of pyroxene by an H_2O-rich magma or fluid phase, or more probably olivine ± Ca-rich clinopyroxene accumulation from a high magnesian magma in the dyke-vein system.

(b) The ultramafites, as probable early formed cumulates, provide a valuable constraint on the composition of primitive, possibly primary magma(s) within the plutonic complex. Parental magma(s) in equilibrium with the ultramafic cumulates are constrained as being moderately magnesian (Mg′-values ca. 55 - 60), calcic, with moderate compatible trace element Ni and Cr abundances, moderate silica activity, basic or ultrabasic, hydrous, but vapour undersaturated, and LREE-enriched. Ca-rich clinopyroxene ± olivine ± orthopyroxene ± chrome-spinel ± Fe-Ti oxide are probable liquidus or near liquidus mineral phases for the primitive parental magma(s).

(c) Similarities in modal mineral phases (Ca-rich clinopyroxene ± orthopyroxene ± brown hornblende ± biotite), the character of Ca-rich clinopyroxene (Ca-rich, low Al_2O_3 and progressive Fe-enrichment), and the near continuous variation trends in whole rock geochemistry (eg. AFM and 100 $Mg/(Mg + Fe^{2+})$ variation diagrams) and mineral geochemistry (eg. Ca-rich clinopyroxene, Wo 40.4 - 45.5 : En 40.2 - 48.7 : Fs 8.2 - 16.8 and $Mg/(Mg + Fe)$ = 70.5 - 86.8) geochemistry in the ultramafite, gabbronorite and two-pyroxene diorite units suggests they are comagmatic.

(d) The observed geochemical variation within the plutonic complex is adequately reproduced by relatively simple fractional crystallization hypotheses, although these solutions are far from unique. Differentiation within two-pyroxene rocks appears to have been controlled by Ca-rich clinopyroxene ± olivine ± orthopyroxene fractional crystallization (the main cumulus mineral phases in the ultramafites). Further differentiation within the granitic leucocratic rocks is consistent with Na-rich plagioclase, amphibole and/or minor Fe-Ti oxide, and possibly zircon driven fractionation.

(e) The geochemical similarity between two-pyroxene rocks and later hornblende-bearing rocks despite apparent dissimilarities in emplacement history and modal mineralogy indicate geochemically similar primitive parental magma(s), with an increase in PH_2O in the later magma(s).

(f) The emplacement of accumulative (ultramafite units) rocks prior to, or contemporaneous with, the proposed differentiates (two-pyroxene diorite units) suggests that the accumulative rocks and differentiates are not derived from the same batch of magma, but that replenishment magmas into the plutonic complex were geochemically similar to the early, primitive, parental magma(s) to the ultramafites.

(g) The ordering and emplacement of successive basic or ultrabasic to acidic magmas in the plutonic complex is consistent with possible storage and differentiation of primitive magma(s) in a lower-level reservoir. Transfer of successively more differentiated magmas into the exposed level of the plutonic complex occurring with time.

(h) The limited Fe-enrichment, along with lithological and mineralogical variations within the Brae plutonic complex, are typical of calc-alkaline suites from destructive plate margins (cf. Best and Mercy, 1967; Lopez-Escobar et al., 1979).

(i) The Brae plutonic complex is late- to post-tectonic and was intruded into metamorphic rocks of the East Mainland succession in a probable continental crustal (sialic) setting at about 430 Ma (early Silurian; time scale of Harland et al., 1982).

3.2 Ultramafites within the Aith-Spiggie plutonic complex

3.2.1 Geological setting

The Aith-Spiggie calc-alkaline plutonic complex occupies an extensive area of the central and southern parts of the Shetland mainland (Figure 1.2-2), and crops out from Aith [HU 345 557] in the N, then discontinuously via islands to the SW of the mainland, and to the S, on the eastern side of the Nesting fault between Spiggie [HU 366 176] and Quendale [HU 372 132] (Flinn, 1967; BGS Sheet 128, 1981). In the Aith area, the complex is truncated to the W by the Walls Boundary fault and cut by associated parallel faults to the E.

The plutonic complex ranges in composition from serpentinized dunite to granite (s.s.). Serpentinized dunite, hornblendite, hornblende-biotite diorite are distributed throughout the complex; more felsic rocks (granodiorite, monzonite, hornblende syenite, porphyritic granite) comprise > 75% of the outcrop area. The diorite, granodiorite and monzonite, in places, show evidence of penetrative deformation, with a weak emplacement fabric developed. Xenolithic marginal-facies units to many of the main rock types are also found, particularly the hornblende-biotite diorite, *monzonite and* granite.

The Aith-Spiggie plutonic complex intrudes the Yell Sound (Moine-like), Scatsta, Whiteness and Clift Hills (Dalradian-like) divisions of the East Mainland succession and is unconformably overlain by Middle Devonian (Givetian) ORS sediments (Flinn, 1985) to the E of Scousburgh, (eg. GR: [HU 38 17]). Undeformed rocks of the plutonic complex cross cut foliation in the schists and gneisses of the East Mainland succession and substantially post-date the main regional tectono-metamorphic episode(s). A narrow contact metamorphic aureole is associated with the Aith-Spiggie plutonic complex for much of its outcrop, however, at contacts with the Dunrossness phyllitic group, Clift Hills division more extensive and well-developed thermal effects are apparent. Contact metamorphic minerals near Scousburgh include, sillimanite, andalusite, and kyanite (Flinn, 1967). Contact metamorphic rocks throughout the area show early, partial re-equilibration to regional metamorphic conditions. Contact metamorphism was dynamic, with two stages of aureole development separated by a crenulation cleavage deformation event within the Dunrossness phyllitic group. Subsequent aureole recrystallization and intrusion occurred under relatively static conditions with only late, open folding due to final emplacement of the Spiggie granite. Miller and Flinn (1966) report a K-Ar age of ca. 400 Ma for muscovite from the Scousburgh aureole; this data suggests K-Ar equilibration, after the latest recrystallization/intrusion event, took place in Early Devonian (Siegenian/Gedinnian) times (timescale after Harland et al., 1982).

3.2.2 Details of exposure

3.2.2.1 Scousburgh ultramafite

Serpentinized dunite and layered dunite-clinopyroxenite are exposed in three principal areas within the Scousburgh ultramafite outcrop.

(a) In a 30 m cliff section at Dry Geos, E of Sands of Scousburgh, GR: [HU 3756 1801] and on the hillside immediately to the E, GR: [HU 3747 1805]. Serpentinized dunite, antigorite-serpentinite, talc-carbonate schist and associated tremolite-talc-chlorite schist occur as sheared, phacoidal masses tectonically interdigitated with contact metamorphosed Dunrossness phyllitic group rocks and pink granite.

(b) At Rhu-allen, SW of Scousburgh village, GR: [HU 3768 1785] numerous, isolated exposures of weakly foliated serpentinized dunite trend NW-SE.

(c) S of the Burn of Scousburgh, both on the E and W side of the B9122 road, serpentinized ultramafites are exposed. The main exposures comprise serpentinized dunite, with two small exposures on the N bank of the Neerson tributary of microrhythmic, phase-layered dunite - clinopyroxenite/olivine clinopyroxenite (Figure 3.2-1a). The layering trends NE-SW, is laterally discontinuous, disrupted and folded by the enclosing serpentinized dunite. Monzonite of the Aith-Spiggie plutonic complex crops out 50 m W of the serpentinized ultramafite exposures and a basal conglomerate unit of the Middle Devonian (Givetian) ORS unconformably overlying *the plutonic complex is* well exposed to the E, GR: [HU 38 17].

3.2.2.2 Lu Ness ultramafites

NW of Lu Ness, Hamnavoe, West Burra, GR: [HU 3694 3529] coastal cliff exposures of medium-grained, marginal-facies, xenolithic, hornblende monzodiorite contain about 10, small (<1 m diameter), metasomatically zoned, ultramafite xenoliths (Figure 3.2-1a). The zonal mineralogical sequence within the xenoliths is similar to that for other zoned ultramafic bodies in Shetland (eg. see section 2.7). The outermost zone comprises a biotite-green hornblende assemblage, followed successively by, a tangentially arranged biotite zone, a radially arranged tremolite zone, a tremolite-magnesite-talc zone, and a central, granular talc-magnesite ± antigorite zone.

The contact between psammitic gneissose schists and hornblendic schist of the Collafirth group, Whiteness division, East Mainland succession and the hornblende monzodiorite is well displayed on the W side of Lu Ness. Partial melting and assimilation of the country-rock gneissose schist is apparent over a 10-15 m gradational contact.

3.2.2.3 Sand ultramafites

Serpentinized dunite forms three separate, main outcrops in the Sand area, on the W coast of Sandsound Voe, central Shetland mainland. Outcrop patterns as defined by magnetometer survey are shown on BGS sheet 128 (1981).

(a) Homogeneous, medium-green, serpentinized dunite, disrupted by minor shears, crops out along a narrow, 15 m long, shore section near Springfield croft, GR: [HU 3513 4825]. The serpentinized dunite is enclosed in a coarse-porphyritic granite (s.s.) of the Aith-Spiggie plutonic complex. To the S the granite is sheeted parallel to the country-rock foliation of the Scatsta quartzitic group, Scatsta division, East Mainland succession.

(b) Serpentinized dunite is exposed in a 100 m coastal section near Annsfield croft, GR: [HU 3503 4884]. The ultramafite outcrop extends inland and is defined by a distinct, positive magnetic anomaly. Contacts with the surrounding porphyritic granite (s.s.) are faulted. The ultramafite is also cut by numerous minor faults and a 1.5 m wide quartz-K-feldspar pegmatite sheet.

(c) A large ultramafite body entirely enclosed by granodiorite and granite of the Aith-Spiggie plutonic complex crops out as a single serpentinized dunite exposure near Gresfield croft, GR: [HU 3465 4802]. Field relations of the ultramafite are not known and the extent of its outcrop is defined only by a positive magnetic anomaly pattern.

3.2.2.4 Houlland ultramafites

(a) A minor serpentinized dunite body is exposed in a 9 m long coastal cliff section SE of Quarsdale and S of the main A971 road at GR: [HU 3491 5159]. The ultramafite is fault bounded and spatially associated with granite and acid pegmatite masses of the Aith-Spiggie plutonic complex.

(b) A large, poorly exposed, weakly foliated, serpentinized dunite body occurs on the rounded hills of Roog and Blunk, S of Houlland, with exposures at GR: [HU 8465 5305] and GR: [HU 3481 5291]. Again, the outcrop of the ultramafite is defined only by an extensive, positive magnetic anomaly over the area.

(c) Massive and weakly foliated serpentinized dunite is exposed at GR: [HU 345 533] and GR: [HU 348 581], in the Burn of Houlland area. The ultramafite body, although poorly exposed, is well defined by a large, complex, positive magnetic anomaly system over the area, and by numerous, scattered, serpentinized dunite boulders. The ultramafite is partially enclosed by granite (s.s.) and foliated monzonite of the Aith-Spiggie plutonic complex and cross-cuts gneissose psammites and semipelite granulites of the Yell Sound division (Moine-like), East Mainland succession.

(d) Three minor, serpentinized ultramafite bodies, defined on the basis of their positive magnetic anomaly systems, occur at East Hill of Houlland, GR: [HU 36 54] and are entirely surrounded by Yell Sound division rocks.

3.2.3 Petrography and mineralogy

3.2.3.1 Cumulate features, primary petrography and mineralogy

Ultramafites within the Aith-Spiggie plutonic complex consist of serpentinized dunite and clinopyroxenite, along with various metasomatically altered and metamorphosed derivatives of these lithologies. Although over 95% of the ultramafites are composed of alteration assemblages there is sufficient relic mineralogy and textures, and sufficient original lithological relationships to permit determination of some aspects of the nature of these rocks.

One locality in the Scousburgh ultramafite shows microrhythmic (layers generally < 50 mm thick), cumulate phase layering, with alternating uniform, medium-thick (thickness = 20 mm - 150 mm) dunite and clinopyroxenite, or olivine-clinopyroxenite phase layers (Figure 3.2-1b). The layering is laterally discontinuous, disrupted and irregularly folded. Phase layer contacts are concordant and sharp, but occassional thin (10 - 20 mm) modally graded contacts also occur.

Texturally, the clinopyroxenites are typically medium- to fine-grained (mean crystal diameters = 0.5 - 1.5 mm), anhedral-or subhedral-granular (with mutual interference grain boundaries) adcumulates (Figure 3.2-1c). Clinopyroxene grains are equant in most samples, but inequidimensional tabular crystals in some samples define a planar igneous lamination parallel to phase layer contacts.

Mineralogically, the clinopyroxenite consists of > 95% clinopyroxene with accessory opaque ore mineral (?altered chrome-spinel). The clinopyroxene is a pale-green coloured, low-Al, chrome-diopside (Mg/(Mg + Fe) = 89.2 - 93.8; En 46.1 - 47.5: Wo 47.3 - 49.4: Fs 3.2 - 5.6; Al_2O_3 = 0.10 - 1.98%; TiO_2 = 0.07 - 0.30%; Cr_2O_3 = 0.14 - 0.46%) and is typically clear, unzoned, with fine (001) lamellae exsolution intergrowths (pseudomorphed ?orthopyroxene).

The serpentinized dunites are homogeneous, equigranular, medium- to fine-grained (mean crystal diameters 0.3 - 2.0 mm), with adcumulate-like textures, and anhedral- to subhedral-granular (mutual interference grain boundaries), equant olivine pseudomorphs (Figure 3.2-1d). Original grain boundaries are defined by secondary magnetite and the major serpentine cords. No orientated textures or banding is seen in thin section.

3.2.3.2 Secondary petrography

Clinopyroxenes within the Scousburgh clinopyroxenites are partially replaced at the margins by a granular aggregate of γ-serpentine, tremolite and magnetite. Exsolution lamallae in the clinopyroxene are totally replaced by γ-serpentine. Accessory ?chrome-spinel is replaced by magnetite.

Dunites from various localities within the plutonic complex show an initial static replacement of the original mineralogy resulting in pseudomorphic mesh-textures involving both α-(length fast) and isotropic serpentine (Figure 3.2-1d). Mesh cords are mainly bipartite with narrow isotropic central partings containing strings of magnetite grains and α-serpentine apparent fibres arranged perpendicularly to the central partings. Mesh cores are composed of α-serpentine apparent fibres of different orientations, isotropic serpentine and possible brucite. In the foliated areas of the serpentinized dunites the original mineralogy is replaced by non-pseudomorphic, ribbon-textured α-serpentine (Figure 3.2-1e). The ribbon-textures (where mesh cords of one particular orientation are well developed), vary continuously from the mesh-textures through to examples where sets of bipartite α-serpentine veins subparallel or anastomosing to a single orientation are separated by restricted isotropic or α-serpentine cores.

Within discrete shears zones in the serpentinized dunites early mesh- and ribbon-textures are systematically replaced by interpenetrating (bladed-mat) γ-serpentine (antigorite) textures. The antigorite-serpentinite shear zone assemblages also include minor amounts of talc and magnesite. *Talc* ± tremolite ± magnesite dominated assemblages (steatites) occur in number of shear zones and also overprint early mesh- and ribbon-textures in the serpentinized dunites, but grade into the antigorite-serpentinites.

The zoned ultramafitic xenoliths from Lu Ness, near Hamnavoe, West Burra show no early petrographic details, both original minerals and pseudomorphic serpentine textures are absent. The central cores to some xenoliths show a non-pseudomorphic, interpenetrative (bladed-mat) γ-serpentine, (antigorite) texture and lack any obvious γ-serpentine (antigorite) bastites. Magnesite, talc and magnetite occur as intergranular, accessory phases within the central cores.

3.2.4 Major and trace element geochemistry

Whole-rock major and trace element analyses of two serpentinized dunites BSP2 (64131) and BSP4 (64127) from the Scousburgh ultramafite at GR: [HU 3756 1801] and GR: [HU 3749 1805] are given in Table 3.1-2. Both samples are highly magnesian (MgO = 39.68 and 44.3%; Mg′ = 89.5 and 92.5), with low Al_2O_3 (0.52 and 0.56%), CaO (1.85 and 4.36%) and SiO_2 (45.4 and 45.7%). The samples contain very low abundances of incompatible trace elements (eg. Sr = 52 and 25 ppm; Zr = 4 and 2 ppm; TiO_2 0.09 and 0.08%) and have high compatible trace element contents (eg. Ni = 2273 and 2420 ppm; Cr = 2240 and 2189 ppm). These major and trace element geochemical features are consistent with an olivine-rich peridotite protolith, although the relatively high SiO_2% and CaO% tends to indicate the presence of pyroxene in the original igneous mineralogy. *Alternatively, selective* enrichment in SiO_2% and CaO_x may have occurred during secondary alteration processes, as both samples show no pyroxene bastites. Ce and Nd abundances are approximately equal to chondrite (Ce_N = 1.13; Nd_N = 0.84) and show moderate LREE to MREE enrichment (Ce_N/Nd_N = 1.34).

3.2.5 Summary and conclusions

(a) Primary textures in the ultramafites of the Aith-Spiggie plutonic complex, where preserved, appear exclusively igneous. Cumulate textures and layering indicate the ultramafic rocks are the cumulate products of crystal fractionation. The presence of possible adcumulates and very low abundances of incompatible elements in the ultramafites suggests near attainment of total equilibrium partitioning of elements during open-system crystallization. The observed exsolution textures, with Ca-rich clinopyroxene hosts and ?orthopyroxene daughter lamallae, are consistent with crystallization and equilibration in a plutonic environment.

(b) Parental magma(s) to the ultramafic cumulates must have had olivine, Ca-rich clinopyroxene and maybe chrome-spinel on or near the liquidus. The absence of orthopyroxene and abundance of dunite cumulates gives some qualitative indication of the silica and magnesium activity in the parental magma(s), and point to parental magma(s) undersaturated in silica. Quantitative or semiquantitative estimation of the degree of silica saturation of the parental magma(s) cannot be done since activity-composition relationships for the relevant systems are presently unknown. The high Mg/(Mg + Fe) ratios of cumulus Ca-rich clinopyroxene cores ($\leq$ 93.8) indicate the primitive magnesian nature of the parental magma(s) (Mg′-value $\leq$ 77.7 (76.1 - 79.1); cpx - melt $K_D = 0.23 \pm 0.02$ (Grove and Bryan, 1983), given that the clinopyroxene grains show evidence of possible orthopyroxene exsolution. High Cr abundances in cumulus Ca-rich clinopyroxene ($\leq$ 3147 ppm) are consistent with

Cr abundances in the equilibrium primative parental magma(s) of approximately 315 ppm (cpx - melt K_D = 10; Sun et al., 1979). An absence of primary hydrous phases in both the serpentinized dunite and clinopyroxenites implies relatively low water fugacities in parental magma(s) to the ultramafic cumulates.

(c) The timing and mechanism of ultramafite accumulation and intrusion are poorly constrained within the Aith-Spiggie plutonic complex. Where contacts between ultramafites and the other members of the complex are exposed they are invariably faulted. No small scale intrusive relations are seen, although the ultramafites do appear discordant on a map scale to some of the felsic plutonic rocks, as well as the country-rock foliation trend in a number of places. Nevertheless, the lack of tectonic fabrics in the ultramafites implies emplacement was essentially a non-tectonic event and original textures are consistent with them having been intruded as a magma or liquid-supported crystal mush. Alternatively, some of the ultramafites may have crystallized at some other level in the pluton and then emplaced at approximately their current structural level during intrusion of the main plutonic units.

(d) Secondary alteration of the ultramafites involves a widespread, dominantly static replacement of the original mineralogy resulting, commonly, in near perfect pseudomorphic mesh-textures, involving both γ- and isotropic serpentine. Such serpentine textures are generally held to be composed of lizardite and are a retrograde phenomena (Cressy, 1979; Wicks and Plant, 1979). A late, dynamic, interpenetrative (bladed-mat) γ-serpentine (antigorite) fabric occurs within discrete shear and fault zones, and reworks the static growth. Associated with the antigorite-serpentinite are talc-magnesite and talc-magnesite-tremoline ± chlorite schists. The petrography of these schists can be related to the antigorite-serpentinite lithology in a systematic fashion. The non-pseudomorphic antigorite is believed to be the product of shearing during retrograde metamorphism. Unequivocal, prograde, serpentine textures are absent from the ultramafites within the Aith-Spiggie plutonic complex.

3.3 Ultramafites within the Sandsting plutonic complex

3.3.1 Geological setting

The Sandsting plutonic complex forms the SE portion of the Walls peninsula, is cut by the Walls Boundary fault and intrudes the Middle Devonian (ORS) Walls sandstone formation (Figure 1.2-2). The complex comprises predominantly of granitic and dioritic rock types with minor gabbroic and mela-gabbroic/ultramafic lithological units (Mykura and Phemister, 1976). Age relations between the granitic rock suite and the other plutonic units which comprise the Sandsting plutonic complex consistently indicate that the granitic rocks are younger. However, mafic dykes intrude all the major plutonic units and represent a widespread, late-stage magmatic event. The Sandsting plutonic complex can be divided into the following lithological units, ordered according to apparent relative age (Mykura and Phemister, 1976):

(a) diorite, including mela-microdiorite, biotite- and hornblende-diorite, tonalite, monzonite, gabbro (which form at least two small dyke-like masses within the diorite) and mela-olivine gabbronorite/plagioclase-bearing lherzolite;

(b) granodiorite;

(c) coarse-grained, biotite granite grading locally into 'graphic' granite;

(d) porphyritic granite and microgranite;

(e) porphyritic microgranite and mafic dykes which cut both the plutonic complex and adjoining sediments;

(f) hydrothermal brecciation and scapolitization (cf. Mykura and Young, 1969).

K-Ar radiometric dating of four mineral-separate samples from the plutonic complex give two separate age groupings. Biotites from the Sandsting granite give ages of 338 ± 13 Ma and 343 ± 13 Ma (Miller and Flinn, 1966). Biotite from a granite NE of Culswick, GR: [HU 26 45] gives an age of 367 ± 10 Ma, with hornblende from a diorite at Hestinsetter Hill, GR: [HU 29 45] giving a date of 378 ± 10 Ma (Snelling, in Mykura and Phemister, 1976). The ages quoted here are recalculated according to the IUGS constants given in Dalrymple (1979). Using the timescale of Harland et al., (1982) closure of the K-Ar system occured in late Devonian to *early Carboniferous times*. The significant disparity (about 30 Ma) between the two age groupings possibly reflect a prolonged intrusion history and/or variation in K-Ar closure temperatures for the different materials dated.

3.3.2 Details of exposure

A concentration of large mela-gabbroic/ultramafic boulders close to Stump Farm, GR: [HP 309 456] strongly suggest the presence of an ultramafite outcrop at shallow depth below the drift (Figure 3.3-1). The outcrop of the ultramafite body is defined by a small, positive magnetic anomaly roughly circular in shape and about 40 m in diameter. Unfortunately, the magnetic anomaly is not of high enough amplitude to give any indication of the three dimensional shape of the ultramafic body. Ultramafite boulders are strung out to the W and WSW of the presumed outcrop (Figure 3.3-1). The spread of the boulders is probably the result of an E to W directed ice flow in this area of Shetland.

3.3.3 Petrography and mineralogy

The ultramafite varies from a biotite-plagioclase-bearing lherzolite to a mela-biotite-olivine gabbronorite. Individual boulders show a relatively uniform modal mineralogical composition, modal variation is seen as a gradational colour change over about 10 cm. The variation being produced by the change in relative abundance of mafic minerals against plagioclase. Individual boulders display no igneous lamination or layering suggestive of a cumulate origin. Mykura and Phemister (1976) describe the lithology as resembling a harrisite, but do not detail any preferred olivine orientation indicative of crescumulate growth (harrisitic texture). The lack of a parallel orientation and extension of any of the mineral phases make a comparison with harrisite inappropriate.

The biotite-plagioclase-bearing lherzolites and mela-biotite-olivine gabbronorites are melanocratic and fine- to medium-grained (grain size = 0.3 - 3 mm). Mineralogically, the rocks consist of 35 - 51% modal olivine, 20 - 28% Ca-rich clinopyroxene, 5 - 10% orthopyroxene, 8 - 26% plagioclase, < 3% phlogopite and accessory amounts of Fe-Ti oxide. The majority of the rocks have a uniform, ophimottled poikilitic texture (Figure 3.3-2a and b). Olivine is subhedral, tabular, medium-grained (grain size = 0.5 - 2 mm) and occurs dominantly as a chadacryst phase in pyroxene oikocrysts. Most grains are partially altered to pseudomorphic mesh α- and γ-serpentine. The mesh texture shows simple chords, with central partings of magnetite or isotropic serpentine. Olivine cores occassionally show a very fine symplectite-like magnetite intergrowth and are forsteritic in composition (Fo = 79.8 - 82.2%; CaO = 0.02 - 0.07%; NiO = 0.21 - 0.64%). Ca-rich clinopyroxene and orthopyroxene occur as large (grain size = 1 - 3 mm), anhedral, equidimensional oikocrysts. The Ca-rich clinopyroxene is diopsidic (Wo 43.4 - 45.9: En 45.4 - 48.0: Fs 8.7 - 9.6; Mg/(Mg + Fe) = 82.6 - 84.7; Al_2O_3 = 2.94 - 4.11%; Cr_2O_3 = 0.58 - 1.25%; TiO_2 = 0.58 - 1.73%). The orthopyroxene is bronzite (En = 81.2 - 82.1%; NiO = 0.03 - 0.13%). The plagioclase is subhedral, prismatic, fine-grained (grain size = 0.3 - 1 mm), with continuous normal zoning (bytownite to labradorite; Ab 22.6 - 36.9: An 62.7 - 76.8: Or 0.4 - 0.6) and occurs as chadacrysts or with an intergranular relationship to the other major mineral phases. Strongly pleochroic, reddish-brown phlogopite is an oikocryst phase (Mg/(Mg + Fe) = 83.3 - 84.1; SiO_2 = 38.97 - 40.14% (hydrous); TiO_2 3.73 - 5.59% (hydrous); $Na_2O/(Na_2) + K_2O)$ = 30.98 - 33.44).

In some thin sections olivine and plagioclase crystals show a near continuous grain-size variation from as small as 0.3 mm to 2 mm (?seriate texture). The smaller olivines and plagioclases tend to occur as chadacrysts enclosed in the central portions of the larger poikilitic pyroxenes, with larger olivine and plagioclase grains at the margins. This texture is taken to indicate that, at least a proportion of olivine and plagioclase chadacrysts nucleated and grew in situ. Further growth of the smaller chadacrysts was then prohibited when they became encased in the pyroxene oikocrysts. Some olivine grains, however, appear significantly larger than others (Figure 3.3-2a and b) and seem to represent an early phase of olivine crystallization.

3.3.4 Summary and conclusions

(a) The unaltered nature of the biotite-plagioclase-bearing lherzolites and mela-biotite-olivine gabbronorites strongly suggests they are part of the Sandsting plutonic complex.

(b) The fine- to medium- grained, ophimottled texture and lack of obvious cumulative layering and textural features tends to suggest the ultramafite-gabbronorite *body is intrusive*. Textural evidence indicates that crystallization may have occurred substantially in situ, with the possible exception of the larger olivine grains. However, the absence of exposed outcrop mean speculation as to the geometry, crystallization and emplacement history of the ultramafite-gabbronorite body must remain tentative.

3.4 Ultramafites within the Northmaven plutonic complex

3.4.1 Geological Setting

The late-Caledonian calc-alkaline Northmaven plutonic complex (Mykura and Phemister, 1976; Phemister, 1979), occupies over 130 km^2 in the NW part of the Shetland mainland (Figure 1.2-2). The complex comprises two main miarolitic granophyric granites, the Ronas Hill and Muckle Roe granites, the net-veined Mangaster Voe diorite and the Eastern granite. Emplacement of the members of the plutonic complex occurred in the following order:

(a) early minor basic intrusions and ? lavas;

(b) early granitic ring dykes (Collafirth, Scarfataing and Vementry granites);

(c) diorites and gabbros (Mangaster Voe diorite);

(d) Eastern Granite;

(e) stock-like miarolitic granophyric intrusions (Ronas Hill and Muckle Roe granite);

(f) swarms of NNW- to NNE-trenching dykes (riebeckite-felsites, dolerites, lamprophyres and granophyres).

Within the Mangaster Voe diorites patches of gabbro are widespread and two minor ultramafic - mela-gabbroic bodies occur. The diorites also show variation to granodiorite. The net-veined diorite complex is bounded on the eastern margin by a long narrow dyke-like body of red granophyric granite which is elongate N to S and extend about 14.5 km.

The plutonic complex intrudes Western Gneisses, the Sand Voe unit and the Queyfirth unit and is faulted against the Middle Devonian (Givetian) Esha Ness volcanics (Figure 1.2-2).

The Ronas Hill granite gives a K-Ar biotite age of 365 ± 8 Ma (Miller and Flinn, 1966); recalculated using the new IUGS constants given in Steiger and Jager (1977) and Dalrymple (1979). Using the time scale of Harland et al, (1982) this dates the complex as Late Devonian (Farnennian).

3.4.2 Details of exposure

3.4.2.1 Glussdale Water ultramafite

Biotite-plagioclase-bearing lherzolite to mela-biotite-olivine gabbronorite crops out on the E side of the A970 about 100 to 150 m N of the Sullum turn off. The ultramafite occurs as small blocks within the Mangaster diorite in two separate exposures within the roadcut at GR:[HU 3328 7309] and GR: [HU 3326 7301]. Magnetometer traverses over the area failed to detect any magnetic anomaly associated with a possible ultramafic source intrusive body. The ultramafite is therefore regarded as being minor detached enclaves in the diorite rather than related to any discrete intrusion.

Serpentinized ultramafite crops out about 100 m S of the above localities at GR: [HU 3327 7290] and GR: [HU 3329 7286]. These ultrmafites are strongly deformed and show a penetrative antigorite foliation suggesting that they may be xenoliths of a ultramafic body from the country rock units.

3.4.2.2 Moora Water ultramafite

Mela-biotite-olivine gabbronorite similar to that at Glussdale Water crops out E of the northernmost of the Moora Waters at GR: [HU 3280 7297]. Numerous boulder of the rock mark the possible extent of the ultramafic - mela-gabbroic body.

Again, a magnetometer survey over the immediate area has failed to trace a likely source intrusive body.

Minor pyroxenite xenoliths also occur in a net-veined, medium-grained hornblende diorite on the N slope of Green Ward GR:[HU 3256 7243].

3.4.3 Petrography

The biotite-plagioclase-bearing lherzolites and mela-biotite-olivine gabbronorites are melanocratic, fine- to medium-grained (grain size = 0.02-3 mm) and homogeneous on a decimeter scale. Mineralogically, the rocks comprise 32-46% modal olivine, 20-35% Ca-rich clinopyroxene, 10-15% orthopyroxene, 6.5-25% plagioclase, <3% phlogopite and minor amounts of Fe-Ti oxide. The principal modal variation is in the ratio of plagioclase to pyroxene. The majority of rocks fall within the gabbronorite field, with a small proportion in the plagioclase-bearing ultramafite (lherzolite) field in the olivine-pyroxene-plagioclase triangle (cf. Figure 1.3-1). Textures are uniform, all rocks have an ophimottled poikilitic texture. Olivine is subhedral-enhedral tabular, fine- to medium-grained (grain size = 0.02-1 mm) with a partial alteration to pseudomorphic mesh α-serpentine and magnetite and is forsteritic (Fo = 79.3-80.4%; *Ca* = 0.04-0.35%; NiO = 0.05-0.37%). Olivine is uniformally distributed throughout the rocks and occurs mainly as chadacrysts in pyroxene (Figure 3.3-2 c and d) or with mutual interference grain boundaries against subhedral plagioclase. Ca-rich clinopyroxene and orthopyroxene both occur as large anhedral equidimensional oikocrysts which give the rocks an ophimottled appearance (Figure 3.3-2d). The Ca-rich clinopyroxene is endiopside (Wo 42.4-44.1: En 46.2-47.3: Fs 9.3-10.3; Mg/(Mg + Fe) = 82.1-83.7; Al_2O_3 = 1.05-4.16%, Cr_2O_3 = 0.17-1.16%) and shows normal continuous zoning. The orthopyroxene is bronzite (En = 81.4-82.0%). Both pyroxenes show no observable intergrowth (exsolution) features. Dark mica is also a oikocryst phase enclosing or partially enclosing the other main mineral phases and is a red-brown phlogopite (Mg/(Mg + Fe) = 78.7-82.6; SiO_2 = 36.82-38.84% (hydrous); TiO_2 = 3.63-5.04% (hydrous); $Na_2O/(Na_2O + K_2O)$ = 28.5-32.9). Plagioclase is subhedral, prismatic, medium-grained, with normal continuous zoning (bytownite/labradorite to labradorite; Ab 29.4-44.4: An 55.3-70.2: Or 0.03-0.4) and occurs generally as chadacrysts in pyroxene and phlogopite (Figure 3.3-2e), or with an intergranular relationship with the other major mineral phases.

It should be noted that the olivine and plagioclase chadcrysts enclosed in the poikilitic pyroxene tend to become larger towards the margins of the pyroxene oikocryst. This texture is interpreted as evidence that the crystals nucleated in place and grew from adjacent liquid. Growth of the crystals of the olivine and plagioclase was arrested when they became encased in the enveloping pyroxene.

3.4.4 Summary and conclusions

(a) The pristine nature of the igneous minerals in the ultramafite and mela-gabbronorite blocks indicates the rocks are probably part of the Northmaven plutonic complex, rather than being inclusions of ultramafic country rock.

(b) The relatively fine grain-size, ophimottled texture and homogeneity of individual ultramafite - mela-gabbronorite blocks may suggest that they represent fragments of an early minor intrusive body; later disrupted and incorporated in the net-veined Mangaster diorite.

4 REE discrimination of Shetland ultramafites

The aims of this section are:

(a) to review the REE geochemistry of ultramafites which may occur in orogenic terrains;

(b) to identify from the data any similarities (or differences) which may exist between ultramafites;

(c) to assess the affects of REE mobility and fractionation during alteration processes on ultramafites;

(d) to devise means of discriminating between ultramafites of differing tectonomagmatic affinity using REE, and

(e) to apply the possible REE discriminant methods to selected ultramafites from the Shetland Caledonides.

4.1 Ultramafite REE geochemistry

4.1.1 Introduction

Ultramafites are widespread in orogenic belts, they comprise many different rock types, occur in a variety of field and petrographical associations. Many of these ultramafites consist of only small isolated tectonic blocks, others occur in close spatial association with gabbros, dolerites and pillow basalts, as the basal member of ophiolite complexes, elsewhere they occur as giant massifs covering hundreds of square kilometres. We may expect, therefore, that there is a variety of origins and emplacement histories for such ultramafites. However, frequently deformation and metamorphism makes interpretation of the origin of many ultramafites in orogenic belts extremely difficult and often ambiguous. Not least because the criteria for the discrimination among origins are not, as yet, well established or at least not broadly accepted. A geochemical discriminant that could reduce this ambiguity and uncertainty would be of great value in the study of ultramafites within orogenic belts.

In recent years, various studies have shown that the major and many trace elements are mobile during many alteration processes (eg. Thompson, 1973; Floyd, 1976; Wood et al., 1976; Humphris and Thompson, 1978; Alderton et al., 1980; Humphris, 1984), and are therefore unreliable for discriminant and petrogenetic studies on rocks that have been subject to a degree of alteration. Increasingly discriminant diagrams based upon geochemically immobile, incompatible elements have been an important tool for petrologists in determining the tectonomagmatic provenance of igneous rocks (eg. Pearce and Cann, 1973; Pearce and Norry, 1979; Wood et al., 1979). Relative abundances of selected trace elements (mainly Ti, Hf, Th, Ta, Y, Zr and Nb) and the REE in altered and metamorphosed rocks are frequently used for classification of rocks into particular tectonic setting and for modelling petrogenetic processes.

Within this section the REE have been chosen for investigation as an ultramafite discriminant tool. In some studies of basaltic systems, the REE abundances and chondrite-normalized profile patterns in metamorphosed rocks are essentially identical to those of the presumed unaltered parent (eg. Humphris et al., 1978; Menzies et al., 1977; Kay and Senechal, 1976; Herman et al., 1974; Dungan et al., 1983; Humphris, 1983; Hajash, 1984). The REE are all members of the

Group IIA elements in the periodic table and have very similar physicochemical properties. This uniformity arises from the nature of their electron configuration which gives a stable 3+ oxidation state and a small but steady decrease in ionic radius with increasing atomic number for a given coordination number. The REE have low to intermediate ionic potentials (cf. Loughman, 1969). These characteristics mean the REE may be expected to fulfil one of the fundamental requirements of a geochemical discriminant; that of immobility during alteration processes. The REE are also likely to be useful because, despite the similarities in their geochemical behaviour, these elements are partially fractionated, one from the other, by many petrological processes. Consequently, ultramafites which have differing magmatic histories and possibly differing *tectomagmatic* provenance may tend to have different REE profile characteristics. Analytical and instrumental developments, especially in neutron activation analysis and mass spectrometry, have led to improvements in the accuracy and precision of REE data. Accurate quantitative analysis of the REE, both as a group and individually, is now, routinely done for many ultramafites even when the elements occur at very low concentrations.

The ultramafites, for the sake of description, have been split into a number of generally acceptable categories, or groups. The groups are themselves subdivided into subgroups. Nine ultramafite groups are listed below and these provide a framework for the more detailed account of the REE profile characteristics given in succeeding sections. The ultramafite group and subgroup listing should be regarded only as a working classification to be modified as we learn more about the petrogenesis of these rocks. There maybe a degree of overlap between rocks of two or more groups and between groups and subgroups themselves. In addition, the subdivision of the ultramafites relies to a large extent on interpretations made by different workers. Nevertheless, ultramafite REE profile characteristics are discussed in the following nine groups: (a) Ophiolite complexes; (b) Alpine-type complexes; (c) Oceanic peridotites; (d) Layered complexes; (e) Appinite-type complexes; (f) Continental picrites; (g) Oceanic picrites; (h) Boninites; (i) Peridotitic komatiites.

Three more ultramafite groups have been excluded from the review, (Kimberlites, Alkaline ultramafic complexes and Alaskan-type complexes) *either* because of a lack of available REE data or because the ultramafites are intrinsically linked with stable continental regions, unlikely to be involved in orogenesis.

4.1.2 Ophiolite complexes

4.1.2.1 General

Ophiolite complexes represent one of the most widely recognised groups of ultramafites within orogenic belts. Ophiolite complexes or ophiolite suites are a distinctive assemblage of mafic and ultramafic rocks (cf. Anon, 1972; Miyashiro, 1975; Coleman, 1977). The concensus definition of an ophiolite complex, includes from bottom to top, the following units: (a) an ultramafic mantle sequence consisting of variable proportions of harzburgite, lherzolite and dunite (more or less serpentinized), usually with a metamorphic tectonite foliation;

(b) ultramafic cumulate rocks; (c) cumulate layered gabbros which grade upwards into, (d) high-level isotropic gabbros; (e) a mafic sheeted dyke complex, and (f) a mafic volcanic complex. These rocks are also commonly associated with: (a) an overlying pelagic sedimentary sequence and metalliferous precipitates; (b) podiform chromitite and dunite bodies within the mantle sequence ultramafites, and (c) felsic igneous rocks (plagiogranites), ordinarily within the high-level gabbros.

Recently, Moores (1982) has proposed an expanded redefinition of the ophiolite assemblage to also include the following units: (a) a crystalline basement with a shallow water platform sedimentary sequence deposited unconformably on it; (b) a tectonic unit of thrust sheets and/or melange complex superimposed over the basement; (c) an inverted dynamothermal metamorphic aureole beneath the sole of the ophiolite allochthon, and (d) postemplacement/obduction deposits.

The ophiolite mantle sequence is invariably composed of harzburgite, with irregular podiform masses of dunite and pockets of lherzolite and pyroxenite. However, in some ophiolites, lherzolites make up a significant proportion of the mantle sequence rocks and mainly contain gabbroic segregations. The harzburgites and lherzolites are essentially composed of forsteritic olivine and enstatite-bronzite orthopyroxene, with chrome-diopside clinopyroxene and accessory chrome-spinel. They show variably developed tectonite textures ranging from granular to granoblastic.

Many ophiolites contain an ultramafic cumulate sequence which passes up-sequence into gabbroic cumulates (layered gabbros). The cumulus minerals are olivine, clinopyroxene, orthopyroxene and plagioclase. Two distinct crystallization sequences are observed from ophiolites (Rocci et al., 1975; Pearce et al., 1984). In one, clinopyroxene and occasionally orthopyroxene, usually crystallizes before plagioclase, giving a basal dunite cumulate unit followed up-sequence by cumulate lherzolites and/or wehrlites, norites and gabbros. In contrast, many ophiolite cumulate sequences show plagioclase to have crystallized before pyroxene, and basal dunites are followed up-sequence by cumulate troctolites and gabbros.

Ophiolites can vary greatly in size, occur in a wide variety of tectonic positions within orogenic belts and may be partially dismembered or metamorphosed. They occur commonly as tectonic melanges, olistrostromes, blocks in blueschist melanges, faulted synclines, autochthonous or parautochthonous basement, and large allochthonous sheets (cf. Colman, 1977; BVSP, 1981). Examples of the latter type invariably show a well-developed ophiolite pseudostratigraphy, and include: Marum ophiolite, Papua - New Guinea (Jaques et al., 1983); Samail ophiolite, Oman (Glennie et al., 1973; Alabaster et al., 1982); Bay of Islands ophiolite, Newfoundland (Church and Stevens, 1971; Suen et al., 1979), and Troodos ophiolite, Cyprus (Moores et al., 1973; Gass and Smewing, 1973; Desmons et al., 1980). Well-preserved ophiolite complexes are rare, but occur in both Mesozoic and younger orogenic belts, eg. the Samail ophiolite, Oman (Glennie et al., 1973; Alabaster et al., 1982), and in Palaezoic orogenic belts, eg. the Karmoy ophiolite (Sturt et al., 1980) which occurs in the Appalachian-Caledonian orogen.

Precambrian ophiolites have also been identified, for example in the Pan-African orogenic belt in Morocco (Le Blanc, 1976) and Egypt (Ries et al., 1983).

Ophiolites are widely held to represent detached slices of oceanic crust and lithosphere (Moores and Vine, 1971; Dewey et al., 1973; Church and Riccio, 1974; Kidd, 1977; Dewey and Kidd, 1977). The thickness and petrology of the well-developed ophiolites match, in a general way, our present understanding of oceanic crust. It is, however, generally accepted that ophiolite complexes may have originated in various tectonic settings, including: marginal basins, incipient ocean ridges, major ocean ridges, 'leaky' transform faults and island arcs. There is, however, frequently great difficulty in assigning an ophiolite to its correct plate tectonic setting. In a few example, an autochthonous or parautochthonous ophiolite may be confidently assigned to its correct setting, eg. the 'Rocas Verdes' ophiolite, Andes (Dalziel et al., 1974), which occurs as a back-arc basin complex behind an active destructive plate margin, and the Zambales range, Luzon (Hawkins, 1980), where back-arc or fore-arc oceanic lithosphere is thrust over an adjacent island arc. However, the majority of ophiolites within orogenic belts are wholly allochthonous. Consequently, many factors have to be considered, such as, the present geological setting, internal structure, geochemistry, petrography of the igneous rocks, nature and provenance of overlying sediments, and the tectonics and timing of emplacement, before the original tectonic setting may be deduced. Recently, Pearce et al., (1984) have proposed a two fold subdivision of ophiolites, on the basis of their gross geochemical, petrological and structural characteristics, into supra-subduction zone (SSZ) ophiolites and mid-ocean ridge basalt (MORB) ophiolites. SSZ ophiolites are dominantly thought to have formed by sea-floor spreading in a marginal basin directly above a subduction zone. The MORB ophiolites are thought to be the product of sea-floor spreading at a major oceanic ridge. In terms of the ultramafic rock types associated with SSZ and MORB ophiolites, the SSZ ophiolites are characterised by harzburgite dominated mantle sequences and ultramafic cumulate sequences where pyroxene(s) crystallizes before plagioclase. In contrast MORB ophiolites have mantle sequences with a significant proportion of lherzolite and have ultramafic cumulate sequences where plagioclase crystallizes before pyroxene(s). The MORB ophiolites, because of the lherzolitic nature of the mantle sequence, show similarities with Alpine-type complexes (see section 4.1.3).

4.1.2.2 REE contents

The REE characteristics of Ophiolite complex mantle sequence harzburgites and dunites are as follows (Figure 4.1-1): Ce_N = 0.0013 - 0.542; Sm_N = 0.006 - 0.348; Yb_N = 0.025 - 0.83; Ce_N/Yb_N = 0.011 - 2.368; Ce_N/Sm_N = 0.72 - 3.85; Sm_N/Yb_N = 0.0053 - 0.895 (Montigny et al., 1973; Kay and Senechal, 1976; Menzies, 1976; Suen et al., 1979; Allegre et al., 1980; Noiret et al., 1981; Pallister and Knight, 1981; Prinzhofer and Allegre, 1985; Jahn, 1986). Most mantle sequence harzburgites and dunites have REE abundances lower than chondrite and show variable overall

LREE to HREE fractionation ($Ce_N/Yb_N \leq 1$ and ≥ 1; Figure 4.1-4a). REE profiles tend to show both LREE to MREE enrichment ($Ce_N/Sm_N \geq 1$; Figure 4.1-1) and variable MREE to HREE depletion ($Sm_N/Yb_N \leq 1$, eg. Figure 4.1-1, no. 3, 6 and 9, or $Sm_N/Yb_N \ll 1$, eg. Figure 4.1-1, no. 4 and 5). These features combine to give a characteristically markedly concave-upwards REE profile shape, similar to some Oceanic peridotites (see section 4.1.4), Ophiolite mantle sequence lherzolites (see below) and Alpine-type complex harzburgites and dunites (see section 4.1.3).

The REE characteristics of Ophiolite complex mantle sequence lherzolites are as follows (Figure 4.1-2): Ce_N = 0.0159 - 6.25; Sm_N = 0.043 - 3.72; Yb_N = 0.32 - 1.69; Ce_N/Yb_N = 0.018 - 6.76; Ce_N/Sm_N = 0.074 - 9.447; Sm_N/Yb_N = 0.134 - 4.022 (Menzies, 1976; Suen et al., *1979; McCulloch and Cameron, 1983; Jelínek* et al., 1984; Prinzhofer and Allegre, 1985). The lherzolitic portions of Ophiolite mantle sequences show a great variation REE profile and range from overall REE-enriched to REE-depleted relative to chondrite. The lherzolite REE profiles fall into four categories: (a) uniformally LREE-enriched ($Ce_N/Yb_N \geq 1$; Figure 4.1-4a), shallowly concave-downwards REE profiles (eg. Figure 4.1-2, no. 5); (b) markedly LREE-depleted ($Ce_N/Yb_N \ll 1$; Figure 4.1-4a), shallowly concave-downwards REE profiles (eg. Figure 4.1-2, no. 11 and 12); (c) flat to slightly LREE-depleted REE profiles ($Ce_N/Yb_N \ll 1$; eg. Figure 4.1-2, no. 3, 4 and 6), and (d) markedly concave-upwards, U- or V-shaped REE profiles (eg. Figure 4.1-2, no. 1, 2, 7, 8, 9 and 10), with a LREE to MREE enriched section ($Ce_N/Sm_N > 1$) and a MREE to HREE depleted section ($Sm_N/Yb_N < 1$).

The REE characteristics of Ophiolite complex ultramafic cumulates are as follows (Figure 4.1-3): Ce_N = 0.04 - 0.53; Sm_N = 0.27 - 1.70; Yb_N = 0.24 - 2.10; Ce_N/Yb_N = 0.03 - 0.613; Ce_N/Sm_N = 0.02 - 3.984; Sm_N/Yb_N = 0.121 - 1.671 (Montigny et al., 1973; Menzies, 1977; Prestvik, 1979; Pallister and Knight, 1981; Jaques et al., 1983). All the ultramafic cumulates have similar REE profile shapes and REE abundances mostly less than chondrite. The REE profiles are LREE-depleted ($Ce_N/Yb_N < 1$; Figure 4.1-4a), mostly concave-downwards, with a flat MREE to HREE section ($Sm_N/Yb_N \approx 1$) and a markedly LREE to MREE depleted section ($Ce_N/Sm_N < 1$). Some REE profiles show a significant positive Eu anomaly (eg. Figure 4.1-3, no. 1, 8 and 9) which is attributable to the occurrence of modal cumulus plagioclase in the ultramafic cumulate; plagioclase preferentially encorporates Eu^{2+} relative to the trivalent REE.

4.1.3 Alpine-type complexes

4.1.3.1 General

Alpine-type complexes are widespread in orogenic belts and occur as isolated ultramafic masses dominantly composed of lherzolite and harzburgite, with lesser amounts of dunite and pyroxenite (Thayer, 1967). They are generally interpreted as emplaced in the solid state, have tectonite fabrics, limited variation in modal mineralogy and mineral composition, and refractory major and trace element compositions. These features are consistent with a commonly accepted origin as depleted residues of mantle partial melting and magma genesis (cf. Green and Ringwood, 1967; Irvine and Findlay, 1972; Menzies and Allan, 1974; Dick, 1977; Obata, 1980).

Examples of Alpine-type complexes include the: Trinity peridotite, eastern Klamath Mts., California (Quick, 1981); Rhonda peridotite, Betic Cordillera, Spain (Obata, 1980; Frey et al., 1985); Beni Bouchera complex, Morocco (Loubet et al., 1975), and the Ligurian peridotites, Italy (Ottonello et al., 1979). The main mass of the Trinity peridotite is composed of plagioclase lherzolite, plagioclase harzburgite, lherzolite, harzburgite and dunite. Websterites, wehrlites and clinopyroxenites are less abundant and form dykes or cumulates at the base of gabbroic intrusions. Quick (1981) regards the complex as a diapirically emplaced mass of upper mantle rocks. The Rhonda peridotite is a large (300 km^2) Alpine-type complex and comprises of three principal rock types, garnet lherzolite, spinel lherzolite and plagioclase lherzolite. The complex is surrounded by a contact aureole. Emplacement of the hot, quasi-plastic peridotite body through the lithosphere is thought not to be diapiric, but dominantly tectonic (Obata, 1980; Frey et al., 1985).

Alpine-type complexes appear to have equilibrated under a wide range of different (mantle facies) physical conditions and are considered to have been emplaced by diaparic and/or tectonic processes during orogenesis. However, their original derivation is not wholly understood and may well vary within the group. Many Alpine-type complexes are held to represent fragments of oceanic upper mantle, primarily because of geochemical and mineralogical similarities with some Ophiolite complexes (particularly MORB ophiolites) and many Oceanic peridotites. Conversely, some Alpine-type complexes which are overlain by thick granulite successions (Nicolas and Jackson, 1972; Fountain and Salisbury, 1981) may be lherzolitic subcontinental mantle masses.

4.1.3.2 REE contents

The REE characteristics of Alpine-type complex lherzolites (mostly spinel-bearing) are as follows (Figure 4.1-5): Ce_N = 0.0204 - 1.64; Sm_N = 0.14 - 2.23; Yb_N = 0.365 - 2.57; Ce_N/Yb_N = 0.015 - 0.945; Ce_N/Sm_N = 0.041 - 1.185; Sm_N/Yb_N = 0.13 - 1.491 (Haskin et al., 1966; Frey, 1970; Frey et al., 1971; Philpotts et al., 1972; Loubet et al., 1975, 1976, 1980; Menzies, 1976; Menzies et al., 1977; Dickey et al., 1979; Loubet and Allegre, 1979; Ottonello et al., 1979, 1984; Frey, 1984; Frey et al., 1985). Spinel- and plagioclase-bearing lherzolites all have qualitatively similar REE profile characteristics, with variable overall LREE-depletion relative to HREE ($Ce_N/Yb_N < 1$; Figure 4.1-4b) and a concave-downwards REE profile shape (eg. Figure 4.1-5, no 7, 8 and 9).

The REE characteristics of Alpine-type complex garnet lherzolites are as follows (Figure 4.1-5): Ce_N = 0.003 - 1.227; Sm_N = 0.4 - 2.3; Yb_N = 0.602 - 3.5; Ce_N/Yb_N = 0.267 - 1.274; Ce_N/Sm_N = 0.222 - 1.357; Sm_N/Yb_N = 0.514 - 1.2 (Garmann et al., 1975; Ottonello et al., 1984; Frey et al., 1985). The limited number of published REE data for garnet lherzolites from Alpine-type complexes have similar REE profiles, they show overall LREE-depletion ($Ce_N/Yb_N < 1$; Figure 4.1-4b) and a concave-downwards REE profile shape (eg. Figure 4.1-5, no. 4, 5 and 6).

As a group the garnet lherzolites tend to have higher REE abundances than the spinel lherzolites and plagioclase lherzolites, which are mostly REE-depleted relative to chondrite.

The REE characteristics of Alpine-type complex harzburgites and dunites are as follows (Figure 4.1-5): Ce_N = 0.02 - 0.7; Sm_N = 0.024 - 0.695; Yb_N = 0.029 - 1.004; Ce_N/Yb_N = 0.16 - 1.75; Ce_N/Sm_N = 0.465 - 3.49; Sm_N/Yb_N = 0.08 - 1.625 (Frey, 1970, 1984; Garmann et al., 1975; Menzies et al., 1977; Frey et al., 1985). Most dunites and harzburgites from Alpine-type complexes have REE contents lower than the lherzolites and lower than chondrite levels, and have LREE/HREE abundance ratios less than chondrites ($Ce_N/Yb_N \leqslant 1$; Figure 4.1-4b). Two principal types of chondrite-normalized REE profile are found. One type is generally similar to the lherzolite REE profiles, that is, LREE to MREE depleted ($Ce_N/Sm_N < 1$), with a concave-downwards REE profile shape (eg. Figure 4.1-5, no. 10, and 11). The second type have markedly concave-upwards, U- or V-shaped chondrite-normalized REE profiles ($Ce_N/Sm_N > 1$ and $Sm_N/Yb_N < 1$; eg. Figure 4.1-5, no. 12).

The REE characteristics of Alpine-type complex pyroxenites are as follows (Figure 4.1-5): Ce_N = 0.02 - 5.7; Sm_N = 0.019 - 27.0; Yb_N = 0.06 - 40.16; Ce_N/Yb_N = 0.007 - 0.507; Ce_N/Sm_N = 0.027 - 1.053; Sm_N/Yb_N = 0.064 - 3.6 (Frey, 1970; Dickey et al., 1979; Loubet and Allegre, 1979; Loubet et al., 1980; Obata, 1980; Frey, 1984; Ottonello et al., 1984). The pyroxenites although mineralogically diverse, all have overall LREE-depleted ($Ce_N/Yb_N < 1$; Figure 4.1-4b), concave-downwards REE profiles (eg. Figure 4.1-5, no. 1, 2 and 3). The range of REE abundances for the group is wide, but most pyroxenites have HREE levels above chondrite (both Sm_N and Yb_N generally greater than 1).

4.1.4 Oceanic peridotites

4.1.4.1 General

Ultramafites from an *oceanic* setting mainly comprise of partially or wholly serpentinized, spinel- or plagioclase-bearing harzburgites and lherzolites (Dick, 1978; Hamlyn and Bonatti, 1980; Dick and Fisher, 1983). Spinel harzburgites and spinel lherzolites constitute close to 70% of Oceanic peridotites. Variably altered, plagioclase peridotites have a widespread distribution and constitute about 30% of Oceanic peridotites. Rare, dunites make up less than 0.5% of all dredged Oceanic peridotites. Oceanic peridotites also include amphibole-bearing spinel peridotites; occurring at a few limited localities. Most Oceanic peridotites are tectonised and frequently secondary metamorphic serpentine assemblages preserve original structures and textures. Petrographically and mineralogically Oceanic peidotites closely resemble Alpine-type complex harzburgites and lherzolites (see section 4.1.3), like Alpine-type complexes, and some Ophiolite complexes, Oceanic peridotites range from diopside-poor harzburgites to diopside-rich lherzolites. A mantle origin is generally accepted for Alpine-type complexes and on the basis of their close petrological similarity, oceanic peridotites are also interpreted as partially depleted-mantle material.

Oceanic peridotites have been dredged or drilled from many transform fault/fracture zone systems, eg. Islas Orcadas fracture zone, S. Atlantic (Coish et al., 1979), Vema fracture zone, Atlantic (Frey, 1984), Owen fracture zone, Carlsberg ridge, Indian Ocean (Hamlyn and Bonatti, 1980), and axial rift valley fault scarps along oceanic spreading ridges, eg. Mid-Atlanatic ridge at 45°N (Aumento and Loubet, 1971) and 25°N (Sinton, 1979).

Oceanic peridotites have also been studied from two subaerially exposed, upper mantle derived masses at St Paul's Rocks, equatorial Atlantic (Frey, 1970) and St John's (Zabargad) Island, Red Sea (Bonatti et al., 1981). The St Paul's Rocks are a set of islets located near the intersection of the St Paul's fracture zone and the Mid-Atlantic ridge. St John's (Zabargad) Island is situated on the western margin of the axial trough of the northern Red Sea at the boundary between fully developed sea floor and the zone of continental extension by lithosphere attenuation. The peridotite mass is sited on the St John's fracture zone, a complex deep-seated fracture system which extends on land and is marked by a significant alkaline igneous lineament. At both localities ultramafic rock-types dominantly comprise tectonized spinel lherzolites and amphibole-bearing spinel peridotites, with associated brown hornblende-rich alkaline plutonic rocks and gabbros. The St Paul's peridotites are spatially related to recent alkaline volcanism and consequently may be unrepresentative of the main body of oceanic upper mantle material (Frey, 1970, 1984).

4.1.4.2 REE contents

The REE characteristics of Oceanic peridotites (excluding amphibole-bearing peridotites) are as follows (Figure 4.1-6): Ce_N = 0.0017 - 1.8; Sm_N = 0.009 - 1.93; Yb_N = 0.05 - 2.169; Ce_N/Yb_N = 0.069 - 2.135; Ce_N/Sm_N = 0.13 - 4.28; Sm_N/Yb_N = 0.11 - 1.55 (Shih and Gast, 1971; Shih, 1972; Jibiki and Masuda, 1974; Dostal and Muecke, 1978; Coish et al., 1979; Bonatti et al., 1981, 1983; Sharaskin et al., 1983; Frey, 1984). Oceanic peridotites, excluding the amphibole-bearing peridotites from St Paul's Rocks and St John's Island, have low REE abundances, mostly less than chondrite levels and Ce_N/Yb_N ratios *less than 1* (Figure 4.1-7a). The REE profiles fall into two distinct categories, those with: (a) variably concave-upwards REE profile shapes ($Ce_N/Sm_N > 1$ and $Sm_N/Yb_N < 1$; eg. Figure 4.1-6, no. 2, 3 and 4), and (b) concave-downwards LREE-depleted REE profiles (eg. Figure 4.1-6, no. 1).

The REE characteristics of Oceanic amphibole-bearing peridotites are as follows (Figure 4.1-6): Ce_N = 0.818 - 19.12; Sm_N = 0.41 - 14.5; Yb_N = 0.35 - 4.3; Ce_N/Yb_N = 1.278 - 8.554; Ce_N/Sm_N = 0.97 - 7.17; Sm_N/Yb_N 0.64 - 8.82 (Frey, 1970; Bonatti et al., 1981). The majority of Oceanic amphibole-bearing peridotites have REE abundances greater than chondrite, with Ce_N/Yb_N ratios greater than 1 (Figure 4.1-7a). The REE profiles appear to fall into two overlapping categories, those with: (a) concave-upwards REE profiles, with a flat MREE to HREE section ($Sm_N/Yb_N \approx 1$) and a markedly enriched LREE to MREE section ($Ce_N/Sm_N \gg 1$; eg. Figure 4.1-6, no. 6, 7 and 8), and (b) uniformally LREE-enriched REE profiles (Ce_N/Sm_N > 1 and Sm_N/Yb_N > 1; eg. Figure 4.1-6, no. 6 and 9).

4.1.5 Layered *complexes*

4.1.5.1 General

Ultramafites frequently form a significant part of the cumulus sequence of Layered complexes. Layered complexes are intrusive bodies ranging in size from large, stratiform lopoliths, eg. the Bushveldt complex, S. Africa (Wager and Brown, 1968), to small funnel-shaped intrusions, eg. the Skaergaard complex, E. Greenland (Wager and Brown, 1968; McBirney and Noyes, 1979). Such complexes are characterised by well-developed rhythmic layering, although layering does occur in many other types of ultramafic complex, including Ophiolite complexes, Alpine-type complexes, Alaskan-type complexes, Appinite-type complexes, Alkaline ultramafic complexes and Peridotitic komatiites. The development of rhythmic layering in Layered complexes separates them from minor differentiated intrusive bodies. Layered complexes mainly consist of gabbroic rocks and ultramafites; the ultramafites include pyroxenites, dunites, peridotites and chromatites. Most major Layered complexes are thought to be evolved from parental magmas with tholeiitic affinities, that is magmas containing normative orthopyroxene and no normative nepheline. However, some Layered complexes have alkaline parents and others have similarities to the calc-alkaline suites typical of orogenic plutonic complexes. The tholeiitic character of some parent magmas is indicated by: (a) the geochemical composition of the chill zone rocks; (b) the mineral fractionation trends observed in the layered rocks, particularly the pyroxenes which characteristically vary from magnesium augite + bronzite -> augite + inverted pigeonite -> ferroaugite -> ferrohedenbergite and indicate the primative parental magmas were subalkalic basaltic, picritic basaltic or komatiitic; (c) the essentially tholeiitic late differentiation trend.

Examples of Layered complexes include: Stillwater complex, Canada (Raedeke and McCallum, 1984), Great Dyke, Zimbabwe (Wilson, 1982), Muskox complex, Canada (Irvine, 1980), Skaergaard complex, E. Greenland (Wager and Brown, 1968; McBirney and Noyes, 1979). Most of these major complexes occur in continental and/or subvolcanic situations and are not contemporaneous with orogenesis. However, it has been increasingly realised that Layered complexes are not restricted to regions of stable continental crust or continental subvolcanic environments, but that they also occur in contemporaneous orogenic belts, ie. they may be synorogenic. Examples of synorogenic Layered complexes include the: Fongen-Hyllingen complex, Trondheim, Norway (Wilson et al., 1981); Dawros complex, Connemara, Ireland (Wadsworth, 1982; Bennett and Gibb, 1983); Belhelvie intrusion, Scotland (Ashcroft and Boyd, 1976; Wadsworth, 1982), and the Insch intrusion, Scotland (Clarke and Wadsworth, 1970; Wadsworth, 1982).

4.1.5.2 REE contents

The REE characteristics of ultramafites from Layered complexes are as follows (Figure 4.1-8): Ce_N = 0.45 - 11.78; Sm_N = 0.33 - 3.73; Yb_N = 0.478 - 9.478; Ce_N/Yb_N = 0.417 - 4.333;

Ce_N/Sm_N = 0.48 - 2.99; Sm_N/Yb_N = 0.80 - 2.78 (Haskin and Haskin, 1968; Frey et al., 1971; Potts and Condie, 1971; Balashov and Suschevskaya, 1973). Also shown in Figure 4.1-8 are the range of REE contents in all Layered complex rocks and for chill or border zone rocks. Ultramafites from Layered complexes generally have REE abundances at greater than chondrite levels and flat to moderately LREE-enriched REE profiles ($Ce_N/Yb_N > 1$; Figure 4.1-7b). The REE profile shapes vary from straight (eg. Figure 4.1-8, no. 5 and 3) to moderately concave-downwards ($Ce_N/Sm_N < 1$ and $Sm_N/Yb_N > 1$; eg. Figure 4.1-8, no. 10). In some major Layered complexes, eg. the Skaergaard, Muskox, Bushveldt and Stillwater intrusions, the early cumulates, which includes many ultramafites, also tend to show positive Eu anomalies and flatter REE profiles ($Ce_N/Yb_N \approx 1$) than the presumed parental melt of the chill zone rocks (Haskin and Haskin, 1968; Paster et al., 1974; Kuo and Crocket, 1979).

4.1.6 Appinite-type complexes

4.1.6.1 General

Ultramafites form a distinctive and significant part of many calc-alkaline ultramafic to felsic, or ultramafic to mafic plutonic complexes within orogenic belts. The ultramafic rock types include: dunites, peridotites, pyroxenites, hornblende pyroxenites and hornblende peridotites. The ultramafite bodies have a variety of configurations, but most tend to lie at the margins, or as stock-like masses forming satellites, to the main plutonic complexes. The bodies are generally regarded as being coeval to their associated plutonic complexes and are interpreted as early formed cumulate products of crystal fractionation.

A more detailed account of the field relations and petrology of ultramafites associated with calc-alkaline plutonic complexes is given in Pitcher and Berger (1972) and Pankhurst et al., (1982). Examples of well-described Appinite-type complexes, include the: Garabal Hill-Glen Fyne complex, Scotland, which comprises dunites, wehrlites, clinopyroxenites and some websterites, along with hornblendic variants of these rock types,- associated with gabbros, variable diorites and granodiorites (Nockolds, 1941); Nordre Bumandsfjord complex, N. Norway, which comprises dunites, wehrlite and lherzolites, associated with gabbros (Sturt el al., 1980); Bear Mt. complex, Klamath Mts., California, which comprises dunites, wehrlites, olivine clinopyroxenites and hornblende clinopyroxenites, associated with hornblendites, gabbros, diorites and granodiorites (Snoke et al., 1981); Big Jim complex, Washington Cascades, USA, which comprises dunites, wehrlites, olivine hornblendites and hornblende websterites, associated with gabbronorite, hornblende gabbro, diorite and granodiorite (Kelemen and Ghiorso, 1986).

Appinite-type complexes associated with calc-alkaline plutons are characteristically developed above subduction zones in a destructive plate margin setting and may be either syn- or post-tectonic.

Snoke et al. (1981, 1982) has emphasized the similarities between Appinite-type complexes and Alaskan-type complexes from the western North American Cordillera (Irvine, 1967, 1974). The

Alaskan-type complexes comprise of variably sized ultramafic bodies with a crude concentric zonal arrangement from a dunite core to outer zones of peridotite, olivine pyroxenite, magnetite pyroxenite, hornblende pyroxenite and hornblendite. Most Alaskan-type complexes are small (around 1 km. diameter) and are frequently spatially associated with large gabbroic or dioritic plutonic masses. Discordant dunite, wehrlite, pyroxenite and hornblendite dykes also occur in many Alaskan-type complexes. Rocks of this association occur, for example, in: S.E. Alaska (Irvine, 1967, 1974; Taylor, 1967), the western North American Cordillera (Snoke et al., 1982), the northern Appalachian Mountains (Cawthorn, 1978) and the Urals, USSR (Taylor, 1967). Like the ultramafites of the Appinite-type complexes, those of the Alaskan-type ultramafic complexes are generally regarded as cumulative in origin, with the overall zonation of the complexes most likely reflecting multiple intrusion of successively more mafic magma through the earlier plutonic units. However, in contrast to Appinite-type complexes, they show a marked Fe-enrichment trend characteristic of complexes with a tholeiitic affinity, and the ultramafites tend to post-date associated gabbroic, dioritic and granodioritic members of the plutonic sequence. Alaskan-type complexes occur in a subduction-related arc tectonomagmatic setting.

4.1.6.2 REE contents

The REE characteristics of Appinite-type complexes are as follows (Figure 3.1-12): Ce_N = 4.25 - 15.2; Sm_N = 4.06 - 6.72; Yb_N = 2.26 - 4.7; Ce_N/Yb_N = 0.904 - 6.726; Ce_N/Sm_N = 0.644 - 3.74; Sm_N/Yb_N = 1.404 - 1.948 (Snoke et al., 1981; see section

3.1). Although limited in number, REE profiles from Appinite-type complexes and are consistent and tend to be flat to LREE-enriched ($Ce_N/Yb_N \geqslant 1$; Figure 4.1-11a), with straight or shallowly concave-downwards REE profile shape and REE abundances greater than chondrite (Figure 3.1-12).

4.1.7 Continental picrites

4.1.7.1 General

Picrites are broadly defined as olivine-rich, melanocratic extrusive or high-level intrusive rocks. They frequently comprise of magnesian olivine, magnesian Ca-rich clinopyroxene and plagioclase, together with accessory minerals such as hornblende, biotite-phlogopite, Fe-Ti oxide, apatite, chrome spinel and possibly analcime. Picrites generally contain more olivine (40 - 65%) than basalts, but have too little modal mafic component to be termed ultramafic (s.s.). Geochemically, picrites are typically enriched in MgO (c. 20 -30%) Ni, Cr and comparatively low in SiO_2, Al_2O_3, TiO_2 and Na_2O. Picrites may occur at the base of sills, but also occur as lava flows and small intrusions in which they may be the dominant rock type. Picrites occur in both alkalic and tholeiitic magmatic associations.

Picrites and similar olivine-phyric basaltic lavas are held to be products of olivine accumulation and are most likely to have compositions modified by fractional crystallization. They are, therefore, suspect as primary or parental magmas. However, picrites containing acicular, dendritic and skeletal olivine and possibly pyroxene are thought to be products of rapid crystallization and may have retained their liquid composition, ie. they are possible primitive magmas of picritic composition.

Examples of picrites from a continental setting, ie. associated with continental tholeiitic and continental alkaline magmas, include: (a) satellite dykes and sills associated with the Layered complex of the Great Dyke, Zimbabwe (Cawthorn and Davies, 1982; Wilson, 1982); (b) minor sills and dykes associated with the Bushveldt layered complex, S Africa (Cawthorn and Davies, 1982); (c) the Deccan picrites, India (Krishnamurthy and Cox, 1977); (d) some Scourie dykes, Scotland (Weaver and Tarney, 1981); (e) minor dykes and sills associated subvolcanic layered complexes from the Thulean Tertiary Igneous Province, Hebrides, Scotland (Drever and Johnson, 1967) and W. Greenland (Clarke and Pederson, 1976), and (f) the Baffin Island picritic lavas (Clarke, 1970; O'nions and Clarke, 1972; Francis, 1985).

Although the picrites have been assigned to either a continental or oceaning setting within this section, the separation of the two groups remains tentative and may mean little in petrogenetic and/or tectonomagmatic terms. For example, it has been suggested that the Baffin Island picrites represent the massive extrusion of picrite magma at the initial stages of seafloor spreading that separated W. Greenland from Baffin Island (Clarke and Upton, 1971).

4.1.7.2 REE contents

The REE characteristics of Continental picrites are as follows (Figure 4.1-9): Ce_N = 10.12 - 22.9; Sm_N = 4.78 - 21.87;

Yb_N = 2.08 - 10.48; Ce_N/Yb_N = 2.185 - 5.97; Ce_N/Sm_N = 1.047 - 2.284; Sm_N/Yb_N = 1.765 - 2.3 (Arth et al., 1977; Weaver and Tarney, 1981). REE data for Continental picrites are limited, with full REE profiles available only for tholeiitic picrites from (a) the Scourie dykes, Scotland (Weaver and Tarney, 1981) and, (b) the (?continental) Archean komatiite province of the Barberton Mt greenstone belt, S Africa (Arth et al., 1977). Nevertheless, picrites from both localities show similar REE characteristics, they have REE abundances enriched relative to chondrite and moderately LREE-enriched REE profiles (Ce_N/Yb_N >1); Figure 4.1-11a). The REE profile shapes vary from straight (eg. Figure 4.1-9, no. 2, 3, 4, 5 and 6) to moderately concave-downwards ($Ce_N/Sm \approx 1$ and $Sm_N/Yb_N > 1$; eg. Figure 4.1-9, no.1).

4.1.8 Oceanic picrites

4.1.8.1 General

Picrites with similar petrological, major and trace element geochemical features to that described in section 4.1.7 are also occasionally found in a mid-oceanic tectonomagmatic environment. Oceanic picrites are mostly of tholeiitic affinity and may include some high-Mg tholeiites (oceanites). Examples of oceanic picrites include: (a) the FAMOUS picrites, from a transition ridge segment at MAR 36°N (Le Roex et al., 1981); (b) tholeiitic picrites from the N. Atlantic, DSDP leg 37, hole 332B, with MgO = 11.5 - 24.3% and $Mg/(Mg + Fe^{2+})$ = 0.67 - 0.83; (Blanchard et al., 1976), and (c) picrites from the Reykjanes transitional ridge segment, N. Atlantic (Wood et al., 1979).

4.1.8.2 REE contents

The REE characteristics of oceanic picrites are as follows (Figure 4.1-9): Ce_N = 4.4 - 5.01; Sm_N = 4.74 - 5.00; Yb_N = 5.38 - 5.98; Ce_N/Yb_N = 0.756 - 0.874; Ce_N/Sm_N = 0.92 - 1.002; Sm_N/Yb_N = 0.814 - 0.898 (Blanchard et al., 1976). Oceanic picrites have REE abundances greater than chondrite. The chondrite-normalized REE profiles show slight, overall LREE-depletion ($Ce_N/Yb_N < 1$; Figure 4.1-11a) and have straight REE profile shapes (eg. Figure 4.1-9, no. 7-10).

4.1.9 Boninites

4.1.9.1 General

Boninites are primitive, high MgO (100 $Mg/(Mg + Fe^{2+}) > 70.0$), intermediate SiO_2, high Ni and Cr, low TiO_2 extrusives (cf. Dietrich et al., 1978; Jenner, 1981; Hickey and Frey, 1982; Cameron et al., 1983; Crawford, 1983). Mineralogically they are quite distinct, being glassy rocks frequently containing Ca-poor pyroxene (eg. clinoenstatite) as an early crystallizing phase and plagioclase being absent. Olivine may be present, with augite or pigeonite commonly as groundmass crystallites (Cameron et al., 1979). Rocks with boninite characteristics have been referred to as magnesian quartz tholeiites, high-Mg andesites or low-Ti ophiolite basalts (eg. Sun and Nesbitt, 1978). Boninites and related rocks have a widespread distribution, a geochemical and mineralogical uniformity. Their distinctiveness from island arc tholeiite and calc-alkaline volcanics suggest they form a unique boninitic or boninite (s.l.) magmatic series.

Modern boninite lavas appear to be restricted to fore-arc areas of oceanic island arcs in the W. Pacific, for example: Mariana - Japan arc (Crawford et al., 1981), Cape Vogel, Papua - New Guinea (Jenner, 1981), Mariana fore-arc and trench (Dietrich et al., 1978), and New Caledonia (Avias, 1976). Rocks with close petrological affinities with boninites also occur in Mesozoic sequences from the eastern Wairarapa, N. Island, New Zealand (Wood, 1980), and Troodos ophiolite, Cyprus (Cameron et al., 1979; Thy, 1984), from the Cambrian Heathcote greenstone belt of central Victoria, Australia (Crawford and Cameron, 1985) and Betts Cove ophiolite, Newfoundland (Coish et al., 1982). Although boninites appear to be associated with fore-arc tectonomagmatic environments, it is not yet clear whether they have resulted from fore-arc magmatism. Nevertheless, boninites may be important markers of fore-arc sequences in ancient volcanic or ophiolite complexes from orogenic belts.

4.1.9.2 REE contents

The REE characteristics of boninites (s.s.) are as follows (Figure 4.1-10): Ce_N = 1.02 - 12.27; Sm_N = 1.16 - 7.53; Yb_N = 1.16 - 4.86; Ce_N/Yb_N = 0.264 - 7.26; Ce_N/Sm_N = 0.47 - 2.254; Sm_N/Yb_N = 0.601 - 3.669 (Dietrich et al., 1978; Sun and Nesbitt, 1978; Jenner, 1981; Hickey and Frey, 1982; Cameron et al., 1983; Sharaskin et al., 1983; Cameron and Crawford, 1985). Boninite REE abundances are all greater than chondrite, most are LREE-enriched (Ce_N/Yb_N > 1; Figure 4.1-11a), with a distinctive shallowly concave-upwards REE profile shape. However, four boninites from the Mariana fore-arc DSDP site 485 do show overall LREE-depletion and have shallowly concave-downwards REE profiles (eg. Figure 4.1-10, no. 5). A small number of boninites from New Zealand and Cyprus also show an overall LREE-depletion (Ce_N/Yb_N < 1), but with the distinctive shallowly concave-upwards REE profile shape (eg. Figure 4.1-10, no. 6 and 7), others have near-symmetrical, concave-upwards REE profiles with minima between Pr and Gd (eg. Figure 4.1-10, no.2).

4.1.10 Peridotitic komatiites

4.1.10.1 General

Peridotitic komatiites or komatiites (s.s) are defined as ultramafic volcanic or hypabyssal rocks, or more specifically lavas or volcaniclastic rocks with > 18% MgO (anhydrous basis). They represent the ultramafic members of the komatiitic magmatic suite (Arndt and Nisbet, 1982). In addition to the high-MgO character, peridotitic komatiites are recognised on the basis of their olivine- and pyroxene-rich primary mineralogies, and by various features indicating an extrusive or high-level intrusive origin - chilled flow tops, polyhedral jointing, well-developed spinifex texture, pillows, fragmental structures (tuffs and breccias) (cf. Donaldson, 1982). Peridotitc komatiites frequently contain a significant proportion of normative feldspar, however, the rocks are ultramafic with olivine, pyroxene and chrome-spinel the only crystalline phases; the feldspar component being contained in the glass phase of the rock. The peridotitic komatiites consist of both cumulate and noncumulate rocks. In cumulate peridotitic komatiites olivine grains are closely packed, solid, subhedral to enhedral and comprise 60 - 80% of the rock. In noncumulate peridotitic komatiites skeletal textures, containing 35 - 60% bladed (spinifex) or embayed (hopper) olivine and pyroxene crystals, are common. In spinifex-free noncumulate rocks olivine and pyroxene may be enhedral or skeletal (40 - 70%). Peridotitic komatiites have MgO content ranging from > 30 to 18% (anhydrous basis) and Mg (Mg + Fe^{2+}) ratios are generally high compared with rocks from other magmatic suites having similar Al_2O_3 contents; TiO_2 contents are low, generally < 1% (anhydrous basis); Ni and Cr are high, > 100 and 140 ppm respectively; CaO/Al_2O_3 ratios are $\ngtr$ 1, although they range between 0.6 to 2.0 (BVSP, 1981; Arndt and Nisbet, 1982).

Peridotitic komatiites have a wide temporal and spatial distribution, but most occur in Archean supracrustal (greenstone) terrains, such as: Abitibi greenstone belt, Ontario, Canada (Pyke et al., 1973: Whitford and Arndt, 1978; BVSP, 1981, p.5-29; Barnes et al., 1983; Arndt, 1986), Belingwe greenstone belt, Zimbabwe (Bickle et al., 1975; Hawkesworth and O'nions, 1977; Nisbet et al., 1977, 1982), Pilbara and Yilgarn blocks, W. Australia (Nesbitt, 1971; Sun and Nesbitt, 1978; Barley and Bickle, 1982; Binns et al., 1982; Arndt and Jenner, 1986), and *Barberton greenstone belt, S. Africa* (Viljoen and Viljoen, 1969; Viljoen et al., 1982; Jahn et al., 1982) Although most common in Archean terrains, peridotitic komatiites also occur in Phanerozoic sequences, for example, they are found on Gorgona Island, Columbia, which is of Tertiary age (Echeverria, 1980, 1982; Aitken and Echeverria, 1984; Echeverria and Aitken, 1986).

The tectonomagmatic setting of peridotitic komatiite magmatism is not well constrained. The available geological evidence shows that at least some Archean peridotitic komatiite were erupted through and onto continental crust in an extensional tectonic setting. The tectonomagmatic setting of the Tertiary komatiites of Gorgona Island is also unclear, but an Oceanic and/or marginal basin setting seems probable.

4.1.10.2 REE contents

The REE characteristics of Tertiary Peridotitic komatiites from Gorgona Island, Columbia are as follows (Figure 4.1-12): Ce_N = 0.327 - 2.71; Sm_N = 1.94 - 5.84; Yb_N = 4.62 - 7.27; Ce_N/Yb_N = 0.053 - 0.38; Ce_N/Sm_N = 0.154 - 0.47; Sm_N/Yb_N = 0.346 - 1.05 (Echeverria, 1980; Aitken and Echeverria, 1984; Echeverria and Aitken, 1986). The peridotitic komatiites and associated picritic tuff breccias have overall LREE-depleted ($Ce_N/Yb_N < 1$; Figure 4.1-11b), concave-downwards REE profiles (eg. Figure 4.1-12, no. 1, 2 and 3), with a flat MREE to HREE section ($Sm_N/Yb_N \simeq 1$) and a LREE to MREE depleted section ($Ce_N/Sm_N < 1$). REE abundances are mostly greater than chondrite. The degree of LREE-depletion, particularly in the LREE to MREE section, in Gorgona peridotitic komatiite is notably greater than for the majority of LREE-depleted Archean peridotitic komatiites (Figure 4.1-12).

The REE characteristics of Archean Peridotitic komatiites from various localities within the Abitibi greenstone belt, Canada, the Yilgarn and Pilbara blocks, W. Australia and the Belingwe greenstone belt, Zimbabwe are as follows (Figures 4.1-12 and 4.1-13): Ce_N = 0.46 - 7.44; Sm_N = 0.97 - 9.09; Yb_N = 1.27

- 8.63; Ce_N/Yb_N = 0.347 - 1.01; Ce_N/Sm_N = 0.309 - 1.06; Sm_N/Yb_N = 0.708 - 1.562 (Arth et al., 1977; Hawkesworth and O'nions, 1977; Whitford and Arndt, 1977; Sun and Nesbitt, 1978; BVSP, 1981; Barnes et al., 1983; Berswick, 1983; S-Seymour et al., 1983; Arndt, 1985; Arndt and Jenner, 1986). REE abundances are generally greater than chondrite, with the MREE to HREE sections of all REE profiles above chondrite levels (Sm_N and Yb_N > 1). Most REE profiles show overall LREE-depletion (Ce_N/Yb_N < 1; Figure 4.1-11b), frequently with a flat MREE to HREE section (Sm_N/Yb_N ≈ 1) and a LREE-depleted LREE to MREE section (Ce_N/Sm_N < 1). These features give most of the Canadian, Australian and Zimbabwian peridotitic komatiites a shallowly concave-downwards REE profile shape (Figure 4.1-12 and 4.1-13).

The REE characteristics of Archean Peridotitic komatiites from various Finnish localities are as follows (Figure 4.1-13): Ce_N = 1.65 - 6.75; Sm_N = 3.02 - 4.8; Yb_N = 1.91 - 3.84; Ce_N/Yb_N = 0.447 - 1.758; Ce_N/Sm_N = 0.475 - 1.406; Sm_N/Yb_N = 0.934 - 1.79 (Jahn et al., 1980). The small number of analysed peridotitic komatiites from Finnish greenstone belts all have REE abundances greater than chondrite. However, there is a degree of variation in the chondrite-*normalized REE* profile characteristics, with two main types recognised: (a) LREE-depleted (Ce_N/Yb_N < 1), concave-downwards REE profiles (eg. Figure 4.1-13, no. 1), with flat MREE to HREE sections (Sm_N/Yb_N ≈ 1) and LREE-depleted LREE to MREE sections (Ce_N/Sm_N < 1), essentially similar to peridotitic komatiites from Gorgona Canada, Australia and Zimbabwe, and (b) LREE-enriched (Ce_N/Yb_N < 1), flat or shallowly concave-downwards REE profiles (eg. Figure 4.1-13, no. 2 and 3), which show similarities with Archean Peridotitic komatiites from the Barberton greenstone belt, S. Africa.

The REE characteristics of Archean Peridotitic komatiites from the Barberton greenstone belt, S. Africa are as follows (Figure 4.1-13): Ce_N = 1.91 - 7.4; Sm_N = 1.89 - 7.48; Yb_N = 1.79 - 4.98; Ce_N/Yb_N = 1.067 - 3.246; Ce_N/Sm_N = 0.932 - 1.8; Sm_N/Yb_N = 1.06 - 1.807 (Sun and Nesbitt, 1978; Jahn et al., 1982). S. African peridotitic komatiites have, in common with most other Archean peridotitic komatiites, REE abundances greater than chondrite. However, they differ significantly in their dominant chondrite-normalized REE profile characteristics. S. African peridotitic komatiites show variable overall LREE-enrichment (Ce_N/Yb_N > 1; Figure 4.1-11b), with either: (a) flat to shallowly concave-upwards REE profiles, with increasing enrichment from HREE to LREE (eg. Figure 4.1-13, no. 7, 8 and 10) and similar to many boninite REE profiles, or (b) shallowly concave-downwards REE profiles (Ce_N/Sm_N < 1 and Sm_N/Yb_N > 1); eg. Figure 4.1-13, no. 9) similar to some LREE-enriched Finnish peridotitic komatiites.

4.2. REE mobility during serpentinization of ultramafic rocks.

When considering the REE chemistry of an ultramafic rock in any petrogenetic or 'fingerprinting' study it is important to evaluate the REE chemical effects of late stage alteration processes. Because of the low REE abundances of many ultramafic rocks (see section 4.1) mobilization of REE during secondary alteration is likely to play a significant role in determining the final REE profile of the rock. Consequently, any petrogenetic hypothesis or fingerprinting model produced may be erroneous.

This section of the thesis investigates the control exerted by hydrous alteration processes, dominantly serpentinization, on the bulk rock REE chemistry of ultramafites.

The problem of REE mobility during serpentinization of ultramafic rocks was first recognised by Frey, (1969). In this work Frey attempted REE mass balance calculations for serpentinized peridotites from the Lizard Complex, comparing bulk rock REE chemistry with analyses of mineral separates and concluded that LREE were removed during serpentinization. However, a recent reappraisal of the work (Frey, 1982) suggests that acid washing of the mineral separates (cf Frey et al., 1978) and analysis of the serpentine may have produced a different conclusion.

Frey et al., (1985) in a study of the Ronda 'high temperature' peridotite found no correlation of REE abundances with degree of serpentinization (<5% to ≈ 30% serpentine). These observations support the assertion by Loubet et al., (1975) that serpentinization does not affect the ultramafic rock REE profile.

Ottonello et al., (1979), using thermodynamic arguments, concluded that the LREE were mobile during serpentinization of

Ligurian peridotites. However, in view of the paucity of appropriate thermodynamic data on REE behaviour during serpentinization such an approach may be premature and ill-founded. Moreover, the Ce anomalies found in some of the peridotites, which Ottonello et al., (1979) sought to explain, may be due to analytical error (Ottonello pers. comm. in Frey, 1982).

Menzies, (1976) also concluded that LREE were mobile and are preferentially removed during serpentinization, but supporting evidence for this conclusion was not presented. Suen et al., (1979) found relative LREE enrichment in a lherzolite from the Bay of Islands ophiolite. This sample (V-13) contains higher abundances of Na, K, Sr and Ba and has an anomalously low bulk rock Mg/(Mg + ΣFe) ratio. These chemical features may be attributable to the presence of kaersutite- and phlogopite-bearing mylonite bands in the sample rather than serpentinization.

Sun and Nesbitt, (1978), in a review of komatiite REE chemistry considered the effects of REE mobility during the hydrous alteration of primary olivine, pyroxene and glass. Their results showed that hydrous alteration has little recognisable control on REE abundances. However, in a number of samples that had undergone extreme alteration, the results demonstrated a preferential mobility of Eu^{2+} occurred. One sample, a completely metamorphosed spinifex-textured peridotitic komatiite from Ravensthorpe has a remarkably erratic REE pattern, particularly at the LREE end. The sample displays large negative Ce and Eu anomalies, a strong unifrom HREE depletion and high total REE abundances. They concluded that this sample had undergone an overall increase in middle REE and La during serpentinization.

REE data for a sequence of three equally spaced samples across the progressively altered border zone of the Preecher Creek 'proto-stratiform' ultramafic intrusion is given in Potts and Condie, (1971). The REE distribution patterns for these three samples converge at the HREE end but have varying amounts of LREE. One sample (37), taken some 60 m from the margin of the intrusion, although highly altered to actinolite from the original cpx-opx-plag-ol assemblage shows no definite change in overall REE profile. Another completely altered ultramafic sample (44), now an actinolite-chlorite schist, that is in contact with the country rock granite gneiss is increasingly enriched in the LREE. Potts and Condie, (1971) suggested that this sample had been contaminated by fluid interaction with the LREE-enriched country rock. It should be noted, however, that alteration of the Preecher Creek intrusion has resulted in actinolite dominated metasomatic assemblages and therefore the accompanying REE mobility observed may not be applicable to cases which involve serpentinization.

Most of the published accounts on the REE chemistry of ultramafic rocks (summarised in Section 4.1) do not consider the possibility of REE mobility and fractionation during serpentinization. Frequently, the regularity of REE found in the ultramafic rock is taken to indicate that they are the original igneous patterns and are thereby discussed on that premise. This assumption appears to be valid for many of the studies, eg. Frey and Suen, (1985), as both serpentinized and non-serpentinized samples show consistent REE chemistries. However, it is clear from the work reviewed above that a rigorous evaluation of the effects of serpentinization on ultramafic rock REE patterns has still to be done. The limited work that has been done tends to be contradictory in that both REE mobility and non-mobility are recorded. One constant feature which can be seen from the review of published data on the REE chemistry of ultramafic rocks is that the degree of secondary alteration and metasomatism tends to be reflected in the relative mobility of REE. Samples which have suffered extreme metasomatic alteration, rather than a 'simple' hydration to serpentine assemblages, are susceptible to REE mobility and late-stage fractionation. Such rocks should be treated with caution in any petrogenetic or 'fingerprinting' study.

4.3. REE mobility during steatitization of ultramafic rocks.

4.3.1. Introduction.

Steatite or soapstone, is the generic name for soft talcose rocks. A wide range of mineralogical compositions maybe covered by these names but the rocks discussed in this section are generally a mixture of talc and carbonates with minor amounts of chlorite, amphibole and opaque minerals. These rocks are the products of advanced metasomatic alteration (steatitization) of ultramafic or serpentinized ultramafic rocks. The degree and kind of alteration can differ considerably but invariable steatitization involves the mobility and transfer of the major element components of the ultramafic proto lith (Jahns, 1967; Curtis and Brown, 1969 and Koons, 1981). Curtis and Brown, (1971) and Koons, (1981) have also shown that certain of the trace elements appear to be mobile during steatitization.

A geochemical comparison of the serpentinized ultramafic rocks and their steatitized alteration products should indicate whether the REE have been mobilized after serpentinization. An observed mobility of the REE would have important consequences for the use of rare earths in petrogenetic and 'fingerprinting' studies of steatitized samples, as it could affect significantly any interpretation. Clearly, it is necessary to evaluate the degree, type and potential for mobility of these elements during the steatitization process.

Rare earth element analytical data for steatite and serpentinized ultramafites from three ultramafic rock occurrences; Cunningsburgh Shetland, Peabody Point, Newfoundland (Rogers et al., 1983) and Tamarak Lake, Trinity County, California (Williams, 1977; Allen and Pennell, 1977) are presented and discussed.

4.3.2. Cunningsburgh, Shetland.

RNAA analyses of REE abundancies in steatite and serpentinized ultramafic samples from Cunningsburgh (see section 2.6) are presented as chondrite-normalized distribution patterns in Figure 4.3-1. The steatite samples are from areas immediately adjacent to the ultramafic sampling sites. The results show several important features of the REE geochemistry of this ultramafic complex.

First, the REE profiles of steatites from Cunningsburgh are variable, sample K2 differs clearly from the other steatite samples in REE content, despite having very similar mineralogy and major element chemistry (see section 2.6 and Appendix A6). The difference may be related to the fact that sample K2 was collected from near (≃ 10 m) the margin of the Cunningsburgh ultramafic complex, or perhaps because it contains chlorite as an accessory mineral.

Second, there is only a broad similarity between the REE profiles of the steatite and its serpentinized ultramafic protolith. Samples K32, K12 and K46 show profiles similar to those of serpentinites BC230 and AC146, though with pronounced irregularities. Sample K2 is in some ways similar to the serpentinized pyroxenite BC41 and may be a severe alteration product of such a rock, although the petrology and major element chemistry of the sample (see Appendix 6 and Table 2.6-4) argue against this idea.

Third, steatite REE profiles show a number of anomalies, that is, individual elements within a profile with markedly different chondrite-normalized concentrations relative to the adjacent REE in the plot (Figure 4.3-1). These observed 'anomalous' elemental concentrations are believed to be real and not a product of analytical errors. Samples, standard rocks and standard solutions within the same batch of analyses (compare K2 with K32, K12 and K46) did not show selective enrichment or depletion of the same REE as might be expected if there was contamination during analysis. Sample K32 and K46 both show sizeable positive Gd anomalies, sample K12 also shows a negative Ho anomaly. Other perturbations on the REE profile cannot be regarded as significant as the variations are not greater than the analytical errors.

4.3.3. Peabody Point, Newfoundland.

REE analysis of serpentinite and its alteration products steatite and a talc-chlorite rock from Peabody Point, Newfoundland (Rogers et al, 1983) are shown as chondrite-normalized distribution patterns in Figure 4.3-2. There is a significant variation in REE abundances from the serpentinite (D) to the several different alteration products. Three different REE profiles appear: sample E-type, sample B-type and sample A/C-type. The talc-chlorite sample (E) shows a moderate depletion in the light REE, La and Ce, and the heavy REE, Yb and Lu, resulting in a concave downwards REE profile. Sample E also shows a small positive Eu anomaly. Conversely, steatite sample B is enriched in La and Lu giving a concave-upward REE profile. Steatite samples A and C have similar profile shapes to the serpentinized ultramafic protolith but are substantially reduced in total REE abundance.

The Peabody Point results suggests steatitization has not only resulted in lower overall REE concentrations in the steatite but has produced selective REE fractionation in some samples.

4.3.4. Tamarack Lake, Trinity County, California.

REE analytical data are given in Figure 4.3-3a & b for metasomatically altered rocks from a serpentinite inclusion in a hornblende diorite intrusive from Tamarack Lake, Trinity County, California (Williams, 1977; Allen and Pennell, 1978). The inset in figure 4.3-3b shows the relative location of the different sample numbers and their positions with respect to the metasomatic alteration zones. The results show the REE are clearly fractionated by the steatitization (Figure 4.3-3a & b). In the inner alteration zones, sample 1 to 4 show a uniform overall loss of REE relative to the serpentinized ultramafic protolith. Both sets of samples show a concave upwards profile shape typical of ultramafites from the lower portions of an ophiolite sequence (see section 4.1). These data indicate a reduction in the total REE abundances, with no selective elemental fractionation during steatitization in the inner alteration zones.

The margin of the ultramafite is placed in the vicinity of sample 5 (Williams, 1977). However, the REE profile for samples 6 and 7 are broadly similar to those of the inner steatite zones (Figure 4.3-3a), it may be that the original boundary was at or around sample 7. Sample 5 shows a slight LREE depletion and reduced total REE abundances relative to the serpentinite. Altered diorite samples 8 and 9 show an enrichment in LREE (Figure 4.3-3b) relative to the hornblende diorite samples HbD and 11. Samples 8 and 9 also show marked positive Eu anomalies. The chloritized hornblende diorite sample 10 is enriched in total REE relative to fresh hornblende diorite (HbD), but shows no selective elemental fractionation (Figure 4.3-3b). Clearly, alteration in these outer zones involves complex REE mobility and variable rare earth elemental fractionation.

4.3.5. Discussion and Conclusions.

It is clear from the three systematic studies outlined here that steatitization involves REE mobility and fractionation, and that the behaviour of the REE in each particular situation is different.

In some Cunningsburgh steatites a number of the REE have anomalous concentrations suggesting that selective elemental fractionation has taken place during the metasomatic process. Normally the REE, because of their similar physicochemical properties, are fractionated from each other on the basis of their ionic radius and consequently normalized patterns are a smoothly varying function of atomic number for a given coordination number. Steatitization at Cunningsburgh appears to involve selected enrichment of Eu and Gd in some samples, with Ho depletion in another. The difference in REE composition between the serpentinized ultramafic rocks and their steatite alteration products is not the result of any primary variation in original ultramafic rock composition but is due to the secondary steatitization. The steatite samples were collected from areas adjacent to the serpentinized ultramafic sampling sites. Petrological, XRF and XRD analysis of the steatite indicates that they were formed from a serpentinized peridotite similar to BC230 and AC146 (see section 2.6). Sample K2 shows a marked enrichment of total REE relative to BC230 and AC146. Other steatites show no meaningful difference in total REE abundances compared to the serpentinized ultramafites. The difference in steatite REE abundances may be due to the fact that K2 may have undergone a degree of REE interaction with nearby metasedimentary phyllites that is not seen in the other steatite samples. Sample K2 also contains chlorite as an accessory *mineral, here chlorite may have* preferentially incorporated REE into its lattice from the metasomatic fluid phase resulting in the peculiar rare earth profile for this rock. Unfortunately, there are no experimentally determined REE partition coefficients available for chlorite and any likely metasomatic fluid which could be used to test the later idea.

At Peabody Point steatitization has resulted in overall depletion of REE in the steatite relative to the original serpentinized ultramafic rock (Figure 4.3-2). The results also indicate that selective REE fractionation has taken place, specifically individual steatites show enrichment in HREE (eg. steatite sample B) and some show a slight depletion in both LREE and HREE compared with the MREE to give a concave downward REE profile (eg. talc-chlorite sample E). In the later case the presence of chlorite in the rock may again be controlling the REE composition of the rock, similar to steatite K2 from Cunningsburgh.

The effects of steatitization on the REE composition of the ultramafic body from Tamarack Lake are different again from those seen at Cunningsburgh (Figure 4.3-1) and Peabody Point (Figure 4.3-2). Steatitization has produced an overall REE depletion, with no selective fractionation of individual REE or groups of REE. In contrast with both Cunningsburgh and Peabody Point chlorite-bearing samples have similar REE profiles to the non-chloritic steatites (Figure 4.3-3 a & b). The presence of chlorite here in these rocks does not appear to affect the steatite REE profile significantly.

It is apparent from these studies that similar steatite-forming alteration processes do not always effect the ultramafic rock REE chemistry in a similar way. Consequently, a knowledge of the type of alteration to which the rock has been subjected may not be enough to predict the behaviour of the REE. It would be necessary to quantatively assess the relative importance of the many complex factors involved in the system of alteration, before using the REE profile of a steatitized ultramafite in any petrogenetic or 'fingerprinting' study. The factors affecting the observed REE content of steatite may be:

(a) The abundance of the REE in the unaltered serpentinite or ultramafic rock, the location and siting of REE ions in or on the mineral phases of the original rock, and the relative stability of these phases during steatitization.

(b) The concentration of the REE in the metasomatising fluid, the partitioning behaviour of the REE between the original mineral phases and the fluid, and the effective transport velocity of the REE out of the system.

(c) The partitioning behaviour of the REE between the secondary steatite mineral phases and the fluid phase.

Obviously, given the number of uncertainties outlined above, the REE chemistry of steatitized ultramafic rocks should be interpreted with extreme caution in any petrogenetic or 'fingerprinting' study. Where they are used the possible REE fractionation effects of the alteration should be fully assessed. Any assessment should entail a detailed knowledge of (a) the primary mineralogy, (b) the likelihood of the REE being incorporated into the steatite minerals and (c) the physicochemical conditions of alteration.

4.4 Ultramafite REE discrimination methods

This section presents four methods of ultramafite discrimination based on REE profile characteristics:

(a) the summary table (section 4.4.1);

(b) the Ce_N/Yb_N diagram (section 4.4.2);

(c) the Ce_N/Sm_N v Sm_N/Yb_N diagram (section 4.4.3);

(d) the multiparameter-condition tree (section 4.4.4).

The discrimination diagrams outlined are applied to selected ultramafites from the Shetland Caledonides. Discrimination results are presented within the section and discussed in detail in section 5.2.

4.4.1 Summary table

REE data for the various ultramafites described in section 4.1 are summarized in Table 4.4-1. The ultramafite REE data in the table are described in terms of seven parameters: Ce_N, Sm_N, Yb_N, Ce_N/Yb_N ratio, Ce_N/Sm_N ratio, Sm_N/Yb_N ratio and profile shape. The ranges and average values relative to chondrite of each of the parameters are given for individual ultramafite groups and subgroups. The table allows a ready comparison to be made between the REE profiles of an ultramafite of unknown origin and those of known affinity.

4.4.2 Ce_N v Yb_N diagram

The degree of LREE to HREE fractionation in ultramafites is readily seen in the Ce_N v Yb_N diagram (Figure 4.4-1). The diagram also describes the overall abundance of REE in the ultramafites. Ce_N monitors the abundance of LREE in the ultramafite, with Yb_N monitoring HREE abundances. Ce is used as a LREE rather than La, because La is not usually determined by isotope dilution. Similarly, Yb is used as a HREE rather than Lu, because Yb is more accurately and widely analysed by the various analytical techniques employed in published sources.

It is clear from Figure 4.4-1 that a considerable overlap exists in the Ce_N v Yb_N diagram between the ultramafite subgroup fields. The main reason for this overlap is that individual REE profiles from different subgroups do, in many cases, have significant REE profile similarities. Nevertheless, the diagram does provide a degree of ultramafite groups or subgroup discrimination.

When applied to selected ultramafites from the Shetland Caledonides the Ce_N v Yb_N diagram shows:

(a) the Brae plutonic complex ultramafite BB212 (64125) falls within the Amphibole-bearing oceanic peridotite field (I), the Appinite-type complex field (K) and on the edge of the Continental picrite field (M);

(b) the Shetland ophiolite mantle sequence harzburgite AU43 (62961) falls within the Ophiolite mantle sequence harzburgite and dunite field (A) alone;

(c) the Shetland ophiolite ultramafic cumulate BU418 (64152) falls within the Ophiolite ultramafic cumulate field (C), the Alpine-type complex lherzolite field (D), the Alpine-type complex pyroxenite field (G) and the Oceanic peridotite field (H);

(d) the Shetland ophiolite ultramafic cumulates BU422 (64153) and BU34 (64149) fall within the Ophiolite mantle sequence harzburgite and dunite field (A), the Ophiolite mantle sequence lherzolite field (B) and the Ophiolite ultramafic cumulate field (C);

(e) the Shetland ophiolite ultramafic cumulate BU37 (64129) falls within the Ophiolite mantle sequence harzburgite and dunite field (A), the Ophiolite ultramafic cumulate field (C) and the Alpine-type complex harzburgite and dunite field (F);

(f) the Dunrossness spilite group serpentinized pyroxenite BC41 (64113) falls within the Appinite-type complex field (K), the Boninite field (N) and on the margins of both the Layered complex ultramafite (J) and South African peridotitic komatiite fields (T);

(g) the Dunrossness spilite group steatite K2 falls within the Ophiolite lherzolite field (B), the Layered complex ultramafite field (J) and on the margin of the Amphibole-bearing oceanic peridotite field (I);

(h) the Dunrossness spilite group serpentinized peridotites BC230 (64779), AC146 (62991), and steatites K12 and K46 fall within or on the margins of the Ophiolite mantle sequence harzburgite and dunite field (A);

(i) one sample, the Dunrossness spilite group steatite K32 falls outside all ultramafite subgroup fields.

4.4.3 Ce_N/Sm_N v Sm_N/Yb_N diagram

Data for published ultramafite REE analyses are shown plotted on a Ce_N/Sm_N v Sm_N/Yb_N diagram in Figure 4.4-2 and the fields covered by the different ultramafite subgroups is shown in Figure 4.4-3. In these diagrams the Ce_N/Sm_N ratio gives a measure of LREE to MREE fractionation and the Sm_N/Yb_N ratio gives a measure of the MREE to HREE fractionation in the ultramafites. Sm is taken as a MREE. It is clear from section 4.1 that many ultramafites REE profiles do not have a constant 'gradient' from LREE to HREE. Frequently, ultramafite REE profiles show significant variation in relative fractionation between the LREE to MREE and the MREE to HREE sections. The Ce_N/Sm_N v Sm_N/Yb_N diagram is principally employed to discriminate ultramafite groups or subgroups which may have similar Ce_N/Yb_N ratios and overall levels of REE, (as monitored by Ce_N and Yb_N) in Figure 4.4-1. In Figure 4.4-3 ultramafites with a Ce_N/Sm_N ratio > 1 and a Sm_N/Yb_N ratio < 1 plot in the bottom, right-hand side, and include, for example, U- or V-shaped, concave-upwards REE profiles typical of many Ophiolite mantle sequence harzburgites. Ultramafites with a Ce_N/Sm_N ratio > 1 and a Sm_N/Yb_N ratio > 1 plot in the top, right-hand side and include those with constant relative enrichment from HREE to LREE typical, for example, of many Boninites, Continental picrites and Appinite-type complexes. Ultramafites with a Ce_N/Sm_N ratio < 1 and Sm_N/Yb_N ratio > 1 plot in the top, left-hand side. Ultramafites with a Ce_N/Yb_N ratio < 1 and Sm_N/Yb_N ratio < 1 plot in the bottom, left-hand side of the diagram, and include those with constant relative depletion from HREE to LREE typical, for example, of many Alpine-type complex lherzolites and Ophiolite ultramafic cumulates.

As in Figure 4.4-1 considerable overlap exists in the Ce_N/Sm_N v Sm_N/Yb_N diagram between the different ultramafite subgroup fields (Figure 4.4-3). However, the Ce_N/Sm_N v Sm_N/Yb_N

diagram does discriminate between some ultramafite subgroups which show a high degree of overlap in the Ce_N v Yb_N diagram (Figure 4.4-1).

Applied to REE data for selected ultramafites from the Shetland Caledonides the Ce_N/Sm_N v Sm_N/Yb_N diagram shows:

(a) the Brae plutonic complex ultramafite BB212 (64125) falls within fields K and I;

(b) the Shetland ophiolite mantle sequence harzburgite AU43 (62961) falls within fields A and B;

(c) the Shetland ophiolite ultramafite cumulate BU418 (64152) falls within fields C, D, G, and H;

(d) the Shetland ophiolite ultramafic cumulates BU34 (64149), BU37 (64129) and BU422 (64153) fall within fields B, C, D, E, F, H and N;

(e) the Dunrossness spilite group serpentinized pyroxenite BC41 (64113) falls within fields J and O-T;

(f) the Dunrossness spilite group steatite K12 falls within fields A, B, F and H;

(g) the Dunrossness spilite group steatite K46 and serpentinized peridotite BC230 (64779) fall within fields N and J, and on the margins of field E;

(h) the Dunrossness spilite group steatite K2 falls within field J, N and M, and on the margin of field I;

(i) the Dunrossness spilite group serpentinized peridotite AC146 (62991) falls within fields H and N, and on the margin of field I;

(j) the Dunrossness spilite group steatite K32 falls outside all ultramafite subgroup fields.

4.4.4 Multiparameter-condition tree analysis

The Ce_N v Yb_N diagram (section 4.4.2) and the Ce_N/Sm_N v Sm_N/Yb_N diagram (section 4.4.3) are examples of discrimination diagrams where two selected parameters provide a degree of discrimination when plotted against each other for ultramafites. However, no single individual or pair of parameters can ever fully analyse and describe the REE profile characteristics of an ultramafite. Analysis of the more complex features requires a modification in our approach to derive the best possible discrimination of ultramafites using REE profiles. It is clear an increased number of parameters are needed if a complete discrimination of ultramafites is to be possible. The chosen approach used is called multiparamter-condition tree analysis (eg. Figure 4.4-4). The tree is a pictorial representation of a sequence of parameters and fractionating conditions. There is no scale, so lengths of lines have no significance. Angles between lines (branches) have no meaning. The tree normally reads from left to right. Parameter nodes are characterised by a single branch input to the node and two or more output branches, each with its own fractionating condition.

The multiparameter-condition tree illustrated in Figure 4.4-4 principally describes the summary data of ultramafite REE profile characteristics given in Table 4.4-1. Parameters within the tree are arranged sequentially, the first three (Ce_N, Sm_N, Yb_N) give a measure of the total REE abundance, the fourth (Ce_N/Yb_N ratio) gives a measure of LREE to HREE fractionation, the fifth (Ce_N/Sm_N ratio) gives a measure of LREE to MREE fractionation, the sixth (Sm_N/Yb_N ratio) gives a measure of MREE to HREE fractionation, and the seventh is the profile shape. The profile shape describes the mutual relations between neighbouring REE on the chondrite-normalized diagram; the relationships are considered to give a concave-upwards, *straight* or concave-downwards shape to the REE profile. Parameters and fractionating conditions which provide no further refinement of the discrimination ability of the tree have been omitted (pruned), leaving only the 'active' parameters. Terminal nodes within the tree show the relevant ultramafite subgroups (see Table 4.4-1) which satisfy the preceding parameter condition alternatives.

In using the tree we start at the left and as we reach a parameter node, moving right, that parameter is calculated for the ultramafite REE profile under investigation. A condition branch is then taken to the next parameter node. The process is continued, moving right step-by-step, until a terminal node is reached. The terminal node will provide a single ultramafite subgroup, or a number of ultramafite subgroups which have similar REE profiles, as the solution.

There are four principal advantages to this kind of analysis:

(a) Complex sequences of parameters and conditions can be analysed using multiparameter-condition trees. All possibilities are defined and considered. The complex REE profile is broken into small parts, then reassembled piece-by-piece to determine the optimum discrimination and analysis procedure.

(b) The approach used provides a better chance of consistent action in achieving ultramafite REE profile discrimination over a series of intermediate parameters.

(c) Just drawing the tree probably forces us to think about the parameters, conditions, etc. in more detail than in less formal methods of analysis.

(d) The important recommendation for use of the multiparameter-condition tree is that it may be the only easy way to treat sequential parameters, given the lack of suitable mathematical and statistical methods.

The multiparameter-condition tree (Figure 4.4-4) when tested against all published ultramafite REE analyses gives the correct classification, at the appropriate terminal node, of over 97% of the data, ie. it is self-consistent. The small number of published ultramafite REE analyses improperly classified in the tree dominantly include samples affected by secondary alteration processes. Many of the ultramafite subgroups share or have overlapping REE profile characteristics and consequently fall on the same terminal point in the tree. Meaningful discrimination on the basis of REE profile characteristics is not possible between these ultramafites using the multiparameter-condition tree.

When applied to selected ultramafites from the Shetland Caledonides the multiparameter-condition tree shows:

(a) the Brae plutonic complex ultramafite BB212 (64125) has REE profile characteristics similar to ultramafite subgroups J, K and M;

(b) the Shetland ophiolite mantle sequence harzburgite AU43 (62961) has REE profile characteristics in common with ultramafite subgroups A, B and H;

(c) the Shetland ophiolite ultramafic cumulates BU34 (64149), BU37 (64129) and BU422 (64153) have REE profiles similar to ultramafite subgroups B, C, D, E, F, G and H;

(d) the Shetland ophiolite ultramafic cumulate BU418 (64152) has REE profile characteristics similar to ultramafite subgroups B, C, D, E and H;

(e) the Dunrossness spilite group serpentinized pyroxenite BC41 (64113) and steatite K2 have REE profile characteristics similar to ultramafite subgroups J, K and M;

(f) the Dunrossness spilite group serpentinized peridotites BC230 (64779), AC146 (62991) and steatite K46 have REE profile characteristics similar to ultramafite subgroups A, B and H;

(g) the Dunrossness spilite group steatite K12 has REE profile characteristics similar to ultramafite subgroups A, B, F and H;

(h) the Dunrossness spilite group steatite K32 has REE profile characteristics similar to ultramafite subgroup D.

5 Summary and Conclusions

The aims of this section are:

(a) to summarize the geological data and conclusions on Shetland ultramafites given in section 2 and 3 of the main body of the thesis;

(b) to provide a comprehensive overall interpretation of the ultramafites within the Shetland Caldonides;

(c) to reinforce, interpret and otherwise clarify the application of REE discrimination methods to Shetland ultramafites given in section 4, and

(d) to summarize, appraise and make recommendations on the general application of the ultramafite REE discrimination methods described in section 4.

5.1 The serpentinized ultramafites of the Shetland Caledonides

5.1.1 Ultramafites within tectonostratigraphic units of the Shetland Caledonides

(a) Geochemical and petrological features of many Shetland Caledonide, serpentinized ultramafites and associated rocks, when viewed in relation to local internal structure/stratigraphy and regional tectonostratigraphy, provide important constraints on the development of the orogenic terrain. The origin of many of the Shetland ultramafites are not only significant points to be considered in any interpretation of the Shetland Caledonides, but should also be regarded in any interpretation of the northern part of the Caledonide-Appalachian orogen as a whole. However, in any wider overall correlation and discussion of the ultramafites of the Shetland Caledonides, assessment needs to be made of their age of formation and the timing and mechanism of emplacement. Such assessment is hampered by uncertainties in tectonostratigraphic correlation, limited knowledge of the individual displacement of tectonostratigraphic units containing the ultramafites and a paucity of age data both on the ultramafites and the tectonostratigraphic units of the Shetland Caledonides. Nevertheless, in the light of these limitations, an attempt has been made to assess at least certain aspects of the tectonic evolution of Shetland Caledonides with particular emphasis on the ultramafite and associated rock assemblages.

(b) The **Western gneisses** (see section 2.1) represent a basement complex of Archean Lewisian gneisses and granulites and forms a northern extension of the Hebridean craton - the Caledonian foreland of the Scottish and Irish Caledonides. The Caledonian foreland in NW Shetland is separated from the complex **Sand Voe unit** (see section 2.2) by a major steeply eastward dipping tectonic discontinuity - the Wester Keolka shear zone - which represents a more-ductile, probably deeper-level, ramp analogue of the orogenic front (Moine thrust zone) seen in N W Scotland. The **Sand Voe unit** comprises of tectonically interleaved Lewisian inlier-like gneisses with numerous ultramafites and Moine-like cover rocks, emplaced at, or ca. 499 Ma. Ultramafites within the Sand Voe unit are petrographically similar to many Archean Lewisian ultramafic bodies from N W Scotland which are thought to represent early, concordant, tholeiitic layered complexes.

(c) On the E side of the Walls Boundary fault the Moine-like Yell Sound division is separated from the Dalradian-like Scatsta division by the Hascosay slide zone (see section 2.3).

Ultramafites within the **Hascosay slide zone** are spatially and structurally associated with possible Lewisian inlier-type gneiss and are interpreted also as Lewisian inliers tectonically emplaced along the ductile thrust system.

(d) The Moine-like Yell Sound division contains an unusual polymictic, matrix-supported, poorly sorted conglomerate horizon, the **Gossabrough polymict conglomerate unit** (see section 2.4). Clast types in the conglomerate include: dunites, peridotites, pyroxenites, basaltic and/or gabbroic rocks, set in a massive arkosic psammite matrix. Taken together matrix and clasts seem to require a nearby source region containing felsic, mafic and ultramafic units. One plausible source could be the Archean Lewisian basement and this would point to emergence and erosion of the basement at the time of Yell Sound division sedimentation.

(e) The status of the **Walls metamorphic series** (see section 2.5) is problematical. The rock unit has a probable pre-Caledonian history, as indicated by radiometric data, and shows significant lithological differences from the Lewisian, Moine and Dalradian successions in Shetland and elsewhere. The series may be a correlative of recently described minor anomalous tectonostratigraphic units within the Moine outcrop of the Scottish Caledonides.

(f) Ultramafites are widespread within Dalradian-like tectonostratigraphic units on the E side (eg. **Scatsta division**, see section 2.7 and 2.8; **Dunrossness spilite group**, see section 2.6) and W side (**Queyfirth unit**, see section 2.9) of the Walls Boundary fault. The **Dunrossness spilite group** is identified as a ca. 590 Ma magmatic sequence developed the culmination of a major basin-deepening sequence within the Dalradian-like portion of the East Mainland succession. Ultramafites within the **Scatsta division** (L. Dalradian) and **Queyfirth unit** (U. Dalradian) are of uncertain origin, but possibly represent pre-, syn- or late-tectonic intrusive masses.

(g) The **Shetland ophiolite** (see section 2.10) is a ca. 470 Ma, supra-subduction zone complex developed in a probable marginal-basin setting after the main Grampian orogenic phase of the Scottish and Shetland Caledonides.

(h) The **Quarff tectonic melange** (see section 2.11) is a late- to post-tectonic fault zone and includes parautochthonous and possible allochthonous rocks. Minor, mylonitized ultramafites within the tectonic melange may plausibly represent tectonically reworked units from the nearby **Dunrossness spilite group**.

5.1.2 Dunrossness spilite group

(a) The Dunrossness spilite group (see section 2.6) is a heterogeneous igneous sequence comformable with the Dunrossness phyllitic group, Clift Hills division of the East Mainland Succession. Lithologies within the Dunrossness *spilite group* include: metabasaltic pillowed and massive lavas, metavolcaniclastites, metavolcaniclastic phyllites, laharic (mud-flow) breccias, metadacitic lavas and tuffs, laminated black graphitic metasediments, massive serpentinized peridotites, spinifex-like textured serpentinized peridotites and serpentinized pyroxenite.

(b) The presence of pillow lavas along with the general facies association indicate a subaqueous, probable marine volcanic/depositional environment for the Dunrossness spilite group. Occassional amygdaloidal metabasalts and the high proportion of volcaniclastic material in the metavolcanic sequences are consist with relatively shallow-water depths (probable < 500 m), but clear indication of insitu pyroclastic activity (magmatic explosivity) is lacking. Some of the metavolcaniclastic units are demonstrably epiclastic, others are autoclastic, but may be the product of non-explosive fragmentation (eg. cooling-contraction granulation). Similar volcaniclastic dominated volcanic sequences are typical of island arc, ocean island or marginal basin regions (Fisher, 1984).

(c) Massive metabasaltic lavas and metabasaltic pillow lavas in the Dunrossness spilite group are variable spilitized, tholeiitic basalts of within-plate tectonomagmatic affinity (continental or ocean island tholeiitic basalts). The two metabasalt suites are not related by high-level fractionation.

(d) Serpentinized peridotites, rare serpentinized pyroxenites, and various alteration products (steatite and antigorite-serpentinites) occur interleaved with metabasaltic lavas, metavolcaniclastites and other metasediments of the Dunrossness spilite group. Some serpentinized peridotites show early, spinifex-like textures of uncertain status.

Whole-rock major element, trace element and REE geochemical characteristics for the serpentinized peridotites are broadly similar to ophiolite mantle sequence harzburgites and are substantially different to peridotitic komatiites. It is clear that field, petrographical and geochemical data do not provide a clear, consistent indication of the tectonomagmatic affinity of serpentinized peridotites.

Cumulate serpentinized pyroxenite from the Dunrossness spilite group shows REE profile characteristics which preclude a direct petrogenetic link with the serpentinized peridotites and are similar to Layered complex ultramafites (see section 4.2 and 5.2.1).

(e) The Dunrossness spilite group is correlated on lithostratigraphic grounds with the lower units of the Southern Highland Group (U. Dalradian) of the Scottish Caldedonides, which are characterised by widespread though sporadic volcanism, eg. the Tayvallich Volcanics. The volcanic units of the Southern Highland Group are of probable lower Cambrian age and this correlates well with a possible igneous crystallization age of 587 ± 15 Ma for a metabasalt from the Dunrossness spilite group. In the Scottish Caledonides the Southern Highland Group volcanism, with pillow lavas and volcaniclastics (Graham, 1976; Harris and Pitcher, 1975; Graham and Bradbury, 1981), is associated with intrusive basic magmatism and prominent development of sill-complexes at Ben Vrackie and Portsoy (Leake, 1982). Serpentinized ultramafites occur within the Portsoy sill-complex and associated with the Tayvallich Volcanics and further emphasis possible similarities with the Dunrossness spilite group on Shetland.

The Dunrossness spilite group volcanism marked the culmination of a major basin-deeping sequence within the

Dalradian-like portion of the East Mainland succession. An analogous tectonostratigraphic sequence is recorded from the Dalradian Supergroup of the Scottish and Irish Caledonides (Harris and Pitcher, 1975; Harris et al, 1978) where increasing tectonic instability culminates in the major Southern Highland Group magmatic episode. The increasing instability is thought to reflect increasing crustal stretching which led to rupture of the Proterozoic Supercontinent (Piper, 1982) and generation of the Iapetus Ocean (Anderton, 1982).

(f) Dunrossness spilite group rocks dominantly show lower-middle amphibolite facies, syn-kinematic metamorphic assemblages. $^{40}Ar/^{39}Ar$ age spectra indicate the peak of the main metamorphic event occur at about 490 Ma, is clearly Caledonian in age and corresponds exactly with the Grampian D3 metamorphic peak at 515 - 490 Ma within the Scottish Caledonides.

(g) Field and $^{40}Ar/^{39}Ar$ radiometric data suggest that a previously unrecognised ca. 461 Ma hornblende gabbro and hornblende diorite intrusive episode occurred within the Dunrossness spilite group outcrop.

5.1.3 Shetland ophiolite

(a) The Shetland ophiolite complex (see section 2.10) is partially dismembered and conforms to the lower part of the consenus model ophiolite pseudostratigraphy. The complex comprises two main allochthonous slices, the upper and lower nappes, with ophiolitic melange units between the upper and lower nappes, below the lower nappe and above the upper nappe.

The lower nappe attains a thickness of about 6.5 km and gives the most complete section through the ophiolite pseudostratigraphy. The lower nappe is composed successively of: mantle sequence harzburgite, an ultramafic cumulate sequence, layered and isotropic gabbro, a sheeted dyke complex and metavolcanic rocks. Formation of the ophiolite is placed at about 470 Ma, with obduction probably occurring very shortly after this time.

(b) Petrological and geochemical characteristics of the complex are typical of an arc-related supra-subduction zone ophiolite.

(c) The ophiolite mantle sequence predominantly consists of harzburgite, with the least refractory being clinopyroxene-bearing. The harzburgites show a distinctive U- or V-shaped REE profile characteristic of depleted mantle sequence rocks from ophiolites. Two tectonite foliations are recognised within the mantle sequence and may reflect two distinct oceanic spreading episodes, or interference of separate spreading centres during the same spreading episode, or a partial overprinting of an early diapiric mantle upwelling foliation by a subsequent lateral oceanic spreading foliation.

(d) In the ultramafic cumulate sequence and gabbro unit the basal cumulate dunites are followed up-sequence by wehrlites, clinopyroxenites and layered gabbros, and corresponds to the crystallization order (ol -> cpx -> plag) typical of island arc tholeiites. Crystallization appears to have been under open-system, steady-state magmatic conditions. The abundance of dunite-chromitite bodies within the mantle and ultramafic cumulate sequences is consistent with expansion of the olivine and chrome-spinel phase volumes under conditions of relatively high pH_2O. Such conditions tend to confirm a subduction-related magmatic environment.

(e) Petrogenetic calculations based on an equilibrium crystallization model estimate the primitive parental magma(s) to the ultramafic cumulates where: (a) highly magnesian, with Mg′-values from 66.2 to 74.8 (63.8 - 76.3); (b) low in incompatible trace elements compared to N-type MORB; (c) high in compatible trace elements compared to N-type MORB; (d) low in total REE abundances with either a flat, shallowly concave-upwards or a moderately LREE-depleted REE profile; (e) low in Na_2O relative to MORB. The absence of cumulus orthopyroxene in the ophiolite probably indicates parental magma(s) was undersaturated in silica.

(f) Basic dykes from the upper portion of the ophiolite pseudostratigraphy are typical island arc tholeiites. Major and trace element variations within the basic dyke suite can be explained in terms of low-pressure, olivine, clinopyroxene and, in the more-evolved rocks, Fe-Ti-oxide controlled crystallization differentiation. Rare, aphyric, high-Mg dykes represent potential parental magma to the more *differentiated* basic dykes and satisfy many of the geochemical features of the modelled primitive parental magma(s) to the ultramafic cumulates.

(g) Metabasaltic hornblende schists within the ophiolitic melange units are interpreted to represent an early period of E-type MORB magmatism and may be remnants of the pre-arc spreading oceanic lithosphere. Formation of this magmatic suite may have been responsible for initial depletion of the mantle sequence prior to the probable marginal (fore- or back-arc) basin extension event which created the main Shetland ophiolite pseudostratigraphy.

(h) The Shetland ophiolite has been interpreted as a remnant of a single supra-Grampian ophiolite sheet responsible for burial and consequent metamorphism of the Grampian tract (Barber and Soper, 1982; Dewey and Shackleton, 1984). However, petrological (Read, 1934; Flinn, 1958; Aziz, 1984) and radiometric age data (Spray, 1984) indicate formation and obduction of the Shetland ophiolite (ca. 470 Ma) significantly post-dates the Grampian D3 metamorphic peak (ca. 515 - 490 Ma; cf. Watson, 1984).

In terms of its main petrological and structural characteristics the Shetland ophiolite does not closely match other ophiolites recognised within the Scottish and Irish Caledonides (cf. Jelinek et al., 1984; Robertson and Henderson, 1984; Hutton et al., 1985) and Scandinavian Caledonides (cf. Furnes et al., 1985). However, the age of the Shetland ophiolite (ca. 470 Ma) compares well with the age of the Bay of Islands complex (475 - 515 Ma; Archibald and Farrar, 1976; Jacobsen and Wasserburg, 1979), Ballentrae (ca. 480 Ma; Thirlwell and Bluck, 1984), Tyrone (ca. 471 Ma; Hutton et al., 1985) and group II Scandinavian ophiolites (Furnes et al., 1985). Consequently, the Shetland ophiolite may represent part of a possible widespread ophiolite formation and obduction episode along the Caledonian system. However, the significant petrological and structural differences between the Shetland ophiolite and the other ophiolite complexes suggests it may have originated as a separate arc-related marginal basin.

5.1.4 Ultramafites within calc-alkaline plutonic complexes of the Shetland Caledonides

(a) Ultramafites associated with calc-alkaline plutonic complexes within Shetland form part of similar post- to late-orogenic, ultramafite-gabbro-granodiorite-granite suites.

(b) Plutonic complexes in the Shetland Caledonides fall into two main groups, respectively E and W of the major transcurrent fault which divides the Shetland Caledonides - the Walls Boundary fault. The eastern complexes give K-Ar ages of $\geqslant$ 400 Ma, are cut by the Walls Boundary fault and Nesting fault and are unconformably overlain by M. Devonian (Givetian) ORS sediments in places. Plutonic complexes of this group include: the Brae plutonic complex (see section 3.1) and the Aith-Spiggie plutonic complex (see section 3.2). The western complexes give K-Ar ages of ca. 350 Ma and cut, or are broadly comtemporaneous with, the ?M. Devonian ORS. Plutonic complexes of this group include: the Sandsting plutonic complex (see section 3.2) and Northraven plutonic complex (see section 3.4).

(c) The gross structural and age differences between the eastern and western plutonic complex groups is also reflected in significant differences in the occurrence and petrology of the ultramafites in the two groups. However, these differences may be an artifact of different erosion level in the respective plutonic groups rather than any fundamental difference in overall composition.

(d) Ultramafites within the Brae (see section 3.1) and Aith-Spiggie (see section 3.2) plutonic complexes show the following characteristics: they comprise of heterogeneous, medium- to coarse-grained, cumulate dunite, peridotites and pyroxenites, with occassional layering; the ultramafites form a sizeable, but minor proportion of the plutonic complex; leucocratic granitic units of the plutonic complex are relatively poorly represented; olivine and Ca-rich clinopyroxene are important cumulus mineral phases within the ultramafites.

(e) Ultramafites within the Sandsting (see section 3.3) and Northmaven (see section 3.4) plutonic complexes show the following characteristics: they are homogeneous, fine- to medium-grained, mela-biotite-olivine gabbronorites or biotite-plagioclase-bearing lherzolites; they lack obvious cumulate features; textural evidence indicates that crystallization occurred substantially insitu; they have near-identical mineral assemblages (olivine (Fo = 79 - 82) - diopsidic clinopyroxene - bronzite - plagioclase (bytownite-labradorite) - Ti-rich phlogopite); the ultramafites are very poorly represented in the plutonic complex as a whole; leucocratic granitic units form a very high proportion of the plutonic complex.

(f) Plutonic complexes E of the Walls Boundary fault (eg. Brae and Aith-Spiggie plutonic complexes) are similar in radiometric age to the bulk of the late- to post-orogenic plutonic complexes within the Scottish Caledonides, which were largely emplaced in the 440 - 400 Ma interval (cf. Sutherland, 1982). Many of the Scottish complexes are associated with penecontemporaneous mafic and ultramafic masses, (Appinite-type complexes) which are preserved as xenoliths, synplutonic dykes or high-level pipes (cf. Pitcher and Berger, 1972; Pankhurst et al., 1982). The Brae and Aith-Spiggie plutonic complexes show lithological, mineralogical and geochemical similarities with many Appinite-type complexes from the Scottish Caledonides, eg. the Garabal Hill - Glenn Fyne complex (Nockolds, 1941), and other areas of the world, eg. the Bear Mt. complex, Klamath Mts. California (Snoke et al., 1981, 1982).

(g) Plutonic complexes W of the Walls boundary fault (eg. Sandsting and Northmaven plutonic complexes) substantially post-date, the main episode of plutonism in the Scottish Caledonides (cf. Sutherland, 1982). Ultramafites associated with western complexes also differ from most Appinite-type ultramafites and may represent minor, penecontemporaneous, 'picrite' intrusive masses.

5.1.5 Brae plutonic complex

(a) Ultramafites within the Brae plutonic complex (see section 3.1) consist of an early heterogeneous suite of cumulate peridotites, pyroxenites and dunites, with combinations of cumulus chrome-diopside, olivine, bronzite, chrome-spinel or Fe-Ti oxide and accessory or minor biotite, brown hornblende and apatite. Ca-rich clinopyroxene is more abundant than orthopyroxene within the ultramafite suite.

(b) Patches of Cu-Ni-Fe sulphide occur in some ultramafites and probably represent the crystallization products of an aggregated immiscible sulphide melt.

(c) Anastomosing dunite and wehrlite dyke-vein systems cross-cutting many massive ultramafites may represent either incongruent dissolution of pyroxene by an H_2O-rich magma or fluid phase, or olivine ± Ca-rich clinopyroxene side-wall accumulations in the dyke-vein system.

(d) The ultramafites pre-date or are broadly contemporaneous with the two-pyroxene diorite and gabbronorite units and were probably emplaced in a crystalline or partially crystalline state to their present structural level within the plutonic complex.

(e) Equilibrium primitive parental magma(s) to the ultramafic cumulates are constrained as being moderately magnesian, calcic, with moderate silica activity (basic or ultrabasic), hydrous but vapour under saturated, LREE-enriched and with moderate compatible trace element (Ni, Cr) abundances. Cpx ± ol ± opx ± chrome-spinel ± Fe-Ti oxide were probable liquidus or near liquidus mineral phases for the primitive parental magma(s).

(f) The petrological consanguinity of ultramafite, gabbronorite and two-pyroxene diorite units in the Brae plutonic complex is strongly supported by similarities in modal mineral phases and near continuous variation in whole rock and mineral geochemistry.

Differentiation in the two-pyroxene plutonic rocks can be explained in terms of cpx ± ol ± opx (the main cumulus mineral phase in the ultramafites) controlled fractional crystallization. Differentiation in the leucocratic granitic rocks is consistent with Na-rich plagioclase, amphibole and/or minor, Fe-Ti oxide and (?)zircon controlled fractional crystallization.

The emplacement of accumulative (ultramafite) units prior to, or contemporaneous with, the proposed comagmatic differentiate (two-pyroxene diorite) units suggests the two are not derived from the same magma batch, but that the replenishment magmas in to the pluton were geochemically similar to the earlier primitive parental magma(s) to the ultramafites. The progressive emplacement of more differentiated magmas into the plutonic system is consistent with differentiation of primitive magma(s) at depth and successive transfer to the higher-level, plutonic complex.

(g) The Brae plutonic complex is late- to post-tectonic and was intruded at about 430 Ma. Lithological, mineralogical and geochemical variation within the plutonic complex is typical of calc-alkaline suites and a continental-crustal (sialic), destructive plate margin setting is probable.

(h) Ultramafites, including dunites, peridotites, pyroxenites, hornblende pyroxenites and hornblende peridotites, form a distinctive and significant part of many calc-alkaline ultramafic-felsic and ultramafic-mafic plutonic complexes within orogenic belts (see section 4.1.6). The Brae plutonic complex shows broad similarities with Appinite-type complexes (Pitcher and Berger, 1972); Pankhurst et al., 1982) and some Alaskan-type complexes (Irvine, 1967, 1974; Taylor, 1967; Perfit, 1980). However, crucial differences exist with Alaskan-type complexes, which show a marked Fe enrichment trend, and gabbro and diorite associated with Alaskan-type complexes are generally interpreted as older than the ultramafites. Appinite-type complexes with close lithological, mineralogical and geochemical similarity to the Brae complex include: Garabal Hill - Glen Fyne complex, Scotland (Nockolds, 1941), Bear Mt. complex, Klamath Mts., California (Snoke et al., 1981, 1982), Big Jim complex, Washington Cascades, USA (Kelemen and Ghiorso, 1986), and Emigrant Gap complex, Sierra Nevada, California (1971).

5.2 REE discrimination of Shetland ultramafites

5.2.1 Application of REE discrimination methods to Shetland ultramafites

It is clear from the results given in section 4.4 that often no unique group or subgroup solution is identified when only a single ultramafite REE discrimination method is used. Each discrimination method has discriminant attributes not shown by the others and represents only a partial solution to the ultramafite REE discrimination problem. Consequently, it is useful to apply each discriminant method to an individual ultramafite REE analysis to achieve optimum discrimination. Results from the application of all three diagramatic ultramafite REE discrimination methods when compounded and a common set of ultramafite groups or subgroups derived frequently give a single ultramafite group or subgroup solution, ie. an ultramafite group or subgroup which satisfies all three ultramafite REE discrimination diagrams is achieved.

Results from application of this compounding procedure to ultramafites from the Shetland Caledonides are as follows:

(a) Brae plutonic complex ultramafite BB212 (64125) is identified as an Appinite-type complex ultramafite (Table 4.4-1, subgroup K);

(b) Shetland ophiolite mantle sequence harzburgite AU43 (62961) is uniquely classified as an Ophiolite mantle sequence harzburgite or dunite (Table 4.4-1, subgroup A).

(c) Shetland ophiolite ultramafic cumulates BU422 (64153) and BU34 (64139) are identified as Ophiolite ultramafic cumulates

(Table 4.4-1, subgroup C) or Ophiolite mantle sequence lherzolites (Table 4.4-1, subgroup B);

(d) Shetland ophiolite ultramafic cumulate BU418 (64153) is identified as an Ophiolite ultramafic cumulate (Table 4.4-1, subgroup C), Alpine-type complex lherzolite (Table 4.4-1, subgroup D) or Oceanic peridotite (Table 4.4-1, subgroup H).

(e) Shetland ophiolite ultramafic cumulate BU37 (64129) is identified as an Ophiolite complex ultramafic cumulate (Table 4.4-1, subgroup C) or Alpine-type complex harzburgite or dunite (Table 4.4-1, subgroup F);

(f) Dunrossness spilite group serpentinized pyroxenite BC41 (64113) and steatite K2 are identified as Layered complex ultramafites (Table 4.4-1, subgroup J);

(g) Dunrossness spilite group steatite K12 is identified as an Ophiolite mantle sequence harzburgite or dunite (Table 4.4-1, subgroup A);

(h) Dunrossness spilite group serpentinized peridotites BC230 (64779) and AC146 (62991), and steatites K46 and K32 do not have a common group or subgroup which satisfies all three ultramafite REE discrimination diagrams.

Where two or more groups or subgroups result from the application of the three diagrammatic ultramafite REE discrimination methods and compounding procedure, meaningful discrimination between the various possibilities is unviable using the discrimination methods in their present form. It should be noted, however, that such ambiguous results may reflect a close similarity in REE characteristics between the group or subgroup possibilities rather than any weakness in the discrimination methods employed.

Application of the ultramafite REE discrimination methods, coupled with the compounding procedure, to Shetland ophiolite ultramafites and the Brae plutonic complex ultramafite give results which support interpretation of these selected ultramafites made on the basis of a number of other considerations, including: present geological setting, internal structure, geochemistry, petrology and the tectonics and mechanism of emplacement (see sections 2.10 and 3.1).

Dunrossness spilite group serpentinized peridotites BC230 (64779) and AC146 (62991), and steatites K46 and K32 do not have a group or subgroup defined in each of all three ultramafite REE discrimination diagrams. The apparent failure of the ultramafite REE discrimination methods and compounding procedure in these cases may well relate to the fact that these altered ultramafites have possibly undergone a degree of secondary REE mobility and fractionation. Both serpentinized peridotites and steatites are metasomatised and comprise significant modal proportion of talc and carbonate. The affects of possible REE mobility and fractionation on Dunrossness spilite group altered-ultramafites mean REE discrimination results for any of the samples should be treated as suspect and interpreted with caution.

5.2.2 Summary and appraisal of the ultramafite REE discrimination methods

(a) The summary table (Table 4.4-1) is a collation of ultramafite REE profile characteristics. It allows a ready qualitative comparison to be made between REE data for an ultramafite of unknown affinity and the various ultramafite groups or subgroups, using the key REE profile parameters: Ce_N, Sm_N, Yb_N, Ce_N/Yb_N ratio, Ce_N/Sm_N ratio, Sm_N/Yb_N ratio and profile shape.

(b) The Ce_N v Yb_N diagram (Figure 4.4-1) has an ultramafite discrimination function base on the overall abundance of REE, as monitored by Ce_N and Yb_N, and the degree of LREE to HREE fractionation (Ce_N/Yb_N ratio). The Ce_N/Yb_N diagram is, therefore, particularly well suited for the differentiation of ultramafite groups or subgroups where significant differences in these particular REE profile parameters exists.

(c) The Ce_N/Sm_N v Sm_N/Yb_N diagram (Figure 4.4-3) has an ultramafite discrimination function based on the degree of LREE to MREE fractionation (Ce_N/Sm_N ratio) and MREE to HREE fractionation (Sm_N/Yb_N ratio). These REE profile parameters are independent of the overall abundance of REE and do not directly reflect the degree of overall LREE to HREE fractionation (Ce_N/Yb_N ratio). However, an ultramafite with both Ce_N/Sm_N and Sm_N/Yb_N ratios less than one must by definition have a Ce_N/Yb_N ratio less than one, and with both Ce_N/Sm_N and Sm_N/Yb_N ratios more than one an ultramafite must have a Ce_N/Yb_N ratio more than one. The Ce_N/Sm_N v Sm_N/Yb_N diagram is primarily used to discriminate between ultramafite groups or subgroups which show significant differences in relative fractionation between the LREE to MREE section and the MREE to HREE section of the REE profile.

(d) The multiparameter-condition tree (Figure 4.4-4) is a pictorial representation of a sequence of parameters and fractionating conditions for analysis of ultramafite REE profiles. Parameters within the tree are arranged sequentially. Ce_N, Sm_N and Yb_N monitor overall REE abundances, Ce_N/Yb_N ratio gives a measure of overall LREE to HREE fractionation. Ce_N/Sm_N ratio and Sm_N/Yb_N ratio give a measure, respectively, of LREE to MREE and MREE to HREE fractionation. The last parameter, REE profile shape, describes the mutual relations between adjacent REE on the chondrite-normalized diagram; the relationships give a concave-upwards, straight or concave-downwards shape to the REE profile. Terminal nodes on the right of the tree indicate the relevant ultramafite groups or subgroups which satisfy the preceding parameter condition alternatives.

(e) Each of the three diagrammatic ultramafite REE discrimination methods described in section 4.4 and outlined above, tends to have discriminant attributes not shown by the others. Therefore, it is recommended that each discrimination diagram should be applied in turn to an ultramafite of unknown affinity in any 'fingerprinting' or discrimination study. Results from the application of all three discrimination diagrams should then be compounded and a common set of ultramafite groups or subgroups defined. When this compounding procedure is applied to ultramafites of known group or subgroup affinity the resultant set always includes the correct group or subgroup and frequently gives a single, correct, ultramafite group or subgroup solution. Where no common set of ultramafite groups or subgroups is defined using the compounding procedure the ultramafite under investigation may have undergone REE mobility and fractionation during secondary alteration processes, eg. Dunrossness spilite group serpentinized peridotite BC230 (64779) (see section 5.2.1).

(f) The low REE abundances in many ultramafites (see section 4.1) means that any mobilization and fractionation of REE during serpentinization is likely to play a significant role in determining the final REE profile characteristics of the rock. Fortunately, most studies have shown that serpentinized and non-serpentinized ultramafite samples from the same body have similar REE geochemistries (see section 4.2). However, care should still be exercised when interpreting the REE profiles of serpentinized ultramafites, since conditions other than those investigated may result in REE mobility and fractionation. If possible the REE geochemical effects of serpentinization should be quantitatively or semi-quantitatively evaluated for the ultramafite being studied. Where REE mobility and fractionation due to serpentinization is recorded in the literature, eg. Sun and Nesbitt (1979), the altered ultramafite invariably shows complete alteration and frequently of a non-pseudomorphic variety.

(g) It is clear from the discussion of the REE mobility and fractionation during steatitzation of ultramafites (see section 4.3) that advanced secondary metasomatic alteration processes can significantly affect the REE discrimination or 'fingerprinting' of altered ultramafites. Geochemical comparison of ultramafites and their various steatitzed alteration products in a number of studies demonstrates that steatitzation involves REE mobility and fractionation and that REE behaviour in each system is different. These observations are further supported by Fowler et al. (1983) in a study of REE distribution after the metasomatic development of a zoned ultramafic body from Fiskenaesset, W. Greenland. In this case varying proportions of all the REE were mobilised and apparently lost during zone generation, with MREE and HREE showing greater mobility than the LREE. Fowler et al. regarded crystal-chemical differences between the precursor assemblage and the zonal minerals as a major controlling factor on the final REE profiles. However, the lack of data on REE patterns of metasomatic minerals, relevant partition coefficients and the variability of REE behaviour during alteration in the different studies even though similar metasomatic minerals were produced means this conclusion may be premature. It seems probable that the resultant REE distribution may have been governed by a number of factors including:

(i) The overall REE abundance in the unaltered serpentinized ultramafite or ultramafite and thereby the rocks igneous petrogenetic history, the distribution of REE in the unaltered rock and sites of concentration in the mineral phases, and the susceptibility of the REE-bearing minerals to alteration.

(ii) The concentration of the REE in the metasomatising fluid, the partition coefficient of the REE between the mineral phases and the fluid, and the ability of the fluid to transport REE out of the system.

(iii) The ability of secondary minerals to take-up the REE released from the original minerals, the relative abundances of secondary minerals and the phase dilution factor.

Because of the potential for REE mobility and fractionation during advanced metasomatic alteration the REE profile characteristics of steatitzed ultramafites should be only interpreted with considerable care.

(h) The ultramafite REE discrimination methods described are substantially empirical in nature, that is, derived from previous data and induction. However, the discrimination methods are not totally divorced from previous knowledge and concepts of ultramafites. Division of the ultramafites into separate groups and subgroups relies heavily on interpretations made by earlier workers and the a posteriori facts of experience rather than merely a priori facts. Consequently, the discrimination methods are likely to be affected by a number of factors, including: lack of data, variable quality of data and errors in the identification of the ultramafites used.

Lack of published REE data for some ultramafite groups and subgroups and sampling bias within others introduces a degree of uncertainty into the ultramafite group and subgroups fields (Figure 4.4-1 and 4.4-3) and branches (Figure 4.4-4) of the discrimination diagrams. In addition some ultramafites have no known REE data and cannot therefore be considered in the ultramafite REE discrimination methods. Nevertheless, the discrimination diagrams are felt to be valid. Where ultramafite group or subgroup fields or branches have been constructed with relatively small datasets, the REE data used is thought to be representative and is consistent with the predicted theoretical REE characteristics for the group or subgroup. For example, REE data for Oceanic picrites is limited, but is consistent with a theoretical picrite composition derived by addition of olivine to N-type MORB, and is thereby held to be representative of that ultramafite group.

The precision and accuracy of ultramafite REE data varies on many levels, with variation between: (a) different published data sources, (b) ultramafite samples within the same data source, and (c) different ultramafite groups and subgroups. The difficulties in analysing REE accurately at very low concentrations mean the experimental errors tend to increase with lower REE abundances. Those ultramafites with REE abundances near the limits of detection for the analytical technique employed are liable to a diminution of both precision and accuracy. These features have important consequences of the construction and application of the ultramafite REE discrimination diagrams, particularly the Ce_N v Yb_N (Figure 4.4-1) and Ce_N/Sm_N v Sm_N/Yb_N (Figure 4.4-3) diagrams. The group and subgroup fields in both the Ce_N v Yb_N and Ce_N/Sm_N v Sm_N/Yb_N diagrams have, therefore, been drawn to allow for experimental errors in the ultramafite data points used. Similarly, application of the discrimination diagrams in any ultramafite REE 'fingerprinting' study should take into account the total range of experimental error in REE data used. Where an ultramafite is on or near a group of subgroup field boundary, or is near the fractionating condition value on a branch of the multiparameter-condition tree, and analytical uncertainties cause a shift into another field or branch, both the alternative solutions should be quoted.

The discriminant ability and validity of all ultramafite REE discrimination methods is dependent on the correct indentification and proper description of individual ultramafites within the various REE data sources used. Where possible, other geological and petrological aspects of each of the ultramafites has been thoroughly investigated to ratify their group or subgroup categorization. Despite the uncertainties and real difficulties in subdividing the ultramafites it is believed the groups and subgroups represent an acceptable working classification scheme on the basis of current knowledge.

(i) Two of the main sources of uncertainty in the construction of the ultramafite REE discrimination methods - the lack of ultramafite REE data and the variable precision and accuracy of available data, could be lessened by: (i) an increased ultramafite REE database, with systematic sampling of ultramafite groups or subgroups with no, or limited REE data and, (ii) the proper standardisation of any additional ultramafite REE data, with analysis by high precision/accuracy RNAA or isotope dilution techniques to minimise experimental errors.

(j) Several other points concerning the REE discrimination of ultramafites in addition to those considered in the foregoing discussions (see section 4 and above) are perhaps worth noting.

(i) Ultramafite samples in any 'fingerprinting' study must be sufficiently large to ensure adequate representation of all minerals in the rock. Even though the quantity used in analysis may be small, this must be taken from a carefully homogenized large sample. The exact sample size will depend on the grain-size and homogeneity of the ultramafite in question, but a minimum 100 g sample is recommended, more when the rock is especially coarse.

(ii) Sampling should be representative of the ultramafite body as a whole. Fresh or partially serpentinized ultramafite samples should be sampled and rocks that have suffered advanced metasomatic alteration (steatitzation) avoided. It may also be useful to analyse progressively more altered ultramafites with a similar igneous petrography, in order to define and quantify the degree of REE mobility and fractionation in the particular system being studied.

(iii) Where no real differences in REE geochemistry exist between one ultramafite group or subgroup and another, it may be that the ultramafites have similar petrogenetic histories. Alternatively, different petrogenetic processes may have produced a convergence of REE characteristics of ultramafite groups or subgroups and that the observed similarities in REE geochemistries are fortuitous.

(iv) Finally, an important point to note, is that, unlike many basalt discrimination diagrams, there is no direct link between groups and subgroups in the ultramafite REE discrimination methods described and particular plate tectonic environments. There is still much more work which needs to be done on ultramafites in general before this could be approached. Ultramafites also suffer from the major problem that they are currently inaccessible to direct sampling in their present day plate tectonic settings. Nevertheless, having identified the affinity of an ultramafite using the ultramafite REE discrimination methods it may be possible to deduct the palaeo-plate tectonic setting indirectly using a number of other considerations, such as: present geological setting, internal structure, nature and provenance of associated rocks, geochemistry, petrology of the igneous rocks and the tectonics and timing of emplacement.

6. References

Aitken, B.G., 1983, Terra Cognita, 3, 148.

Aitken, B.G. & Echeverria, L.M., 1984, Contrib. Mineral, Petrol., 86, 94-105.

Alabaster, T., Pearce, J.A. & Makpas, J., 1982, Contrib. Mineral. Petrol., 81, 168-83.

Alderton, D.H.M., Pearce, J.A. & Potts, P.J., 1980, Earth Planet. Sci. Lett., 49, 149-65.

Allegre, C.J., Brevart, O., Joron, J.L., Minister,J.F. & Noiret, G., 1980, Colloq. Int. C.N.R.S., 272, 125-33.

Allen, P.A., 1982, J. Geol. Soc. Lond., 139, 44-58.

Allen, R.O. & Pennel, S.E., 1978, In Archaeological Chemistry II, Washington, D.C., *American Chemical Society*, *230-257*.

Amin, M.S., 1952, Geol. Mag., 89, 97-105.

Amin, M.S., 1954, Geol. Mag., 91, 399-406.

Anderton, R.J., 1982, J. Geol. Soc. Lond., 139, 142-431.

Anonymous, 1972, Geotimes, 17, 24-25.

Archibald, D.A. & Farrar, E., 1976, Can. J. Earth Sci., 12, 520-529.

Arndt, N.T., 1977, Can. J. Earth Sci., 14, 262-

Arndt, N.T., 1986, J. Petrol, 27 (2), 279-301.

Arndt, N.T., Naldrett, A.J. & Pyke, D.R., 1977, J. Petrol., 18 (2), 319-369.

Arndt, N.T. & Nisbet, E.G., 1982, Komatiites, George Allen & Unwin, London, 526 pp.

Arndt, N.T. & Jenner, G.A., 1986, Chem. Geol., 56, 229-255.

Arth, J.G. & Hanson, G.N., 1975, Geochim. Cosmochem. Acta, 39, 325-62.

Arth, J.G., Arndt, N.T. & Naldrett, A.J., 1977, Geology, 5, 590-4.

Ashcroft, W.A. & Munro, M., 1978, Scott. J. Geol., 14, 55-79.

Aumento, F. & Loubet, H., 1971, Can. J. Earth Sci., 8, 631-663.

Avias, J.V., 1976, In Int. Symp. Geodynamics In New Caledonia, Editions Technip., Paris, 245.

Aziz, R., 1984, unpub. Ph.D. Thesis, University of Liverpool.

Bain, J.A., Briggs, D.A. & May, F., 1971, Trans. Instn. Min. Metall., 80, B, 77-84.

Balashov, Y.A. & Suschevskaya, N.M., 1973, Geokhimiya, 12, 1823-30.

Barley, M.E. & Bickle, M.J., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.) George Allen & Unwin, London.

Barnes, S.-J., Gordon, M.P. & Naldrett, A.J., 1983, Contrib. Mineral. Petrol., 83, 293-308.

Bartholomew, I.D., 1984, unpub. Ph.D. Thesis, Open University, 523 pp.

Balsaltic Volcanism Study Project, 1981, Basaltic Volcanism on the Terrestrial Planets, Pergamon Press Inc., New York.

Bennett, M.C. & Gibb, E.G.F., 1983, J. geol. Soc. Lond., 140, 63.

Bender, J.F. *et al.*, 1978, Earth Planet, Sci. Lett., 41, 277-302.

Beswick, A.E., 1983, Contrib. Mineral. Petrol., 82, 221-231.

Best, M.G., 1975, J. Petrol., 16, 212-36.

Best, M.G. & Mercy, E.L.P., 1967, Amer. Min., 52, 436-74.

Bickle, M.J., 1982, In Komatiite (ed. Arndt, N.T. & Nisbet, E.G.) George Allen and Unwin, London.

Bickle, M.J., Martin, A. & Nisbet, E.G., 1975, Earth Planet Sci. Lett., 27, 155-62.

Bickle, M.J. et al., 1976, Nature, London, 263, 577-80.

Binns, R.A., Hallberg, J.A. and Taplin, J.H., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.) George Allen & Unwin, London.

Blanchard, D.P. *et al.*, 1976, J. Geophys. Res., 81, 4231-4246.

Bonatti, E. *et al.*, 1981, Geology, 9, 474-79.

Bonatti, E. *et al.*, 1983, Earth Planet. Sci. Lett., 62, 229.

Bottinga, Y. & Weill, D.F., 1970, Am. J. Sci., 272, 438-75.

Bott, M.H.P., & Watts, A.B., 1970, Nature, Lond., 225, 265-8.

Boynton, W.V., Staryk, P.M. & Schmidt, R.A., 1976, Geochim. Cosmochim. Acta., 40, 1439.

Bowes, D.R., Wright, A.E. & Park, 1964, J. geol. Soc. Lond., 120, 153-92.

Brady, R., 1977, Geochim. Cosmochim. Acta., 41, 113-25.

Brewer, J.A. & Smythe, D.K., 1984, J. geol. Soc. London., 141, 105-120.

Brent, G. & Dalrymple, G.B., 1979, Geology, 7, 558-560.

Brown, P.E., 1965, Proc. Yorks. geol. soc., 35, 103-38.

Buttler, S.J., 1984, unpub. Ph.D. thesis, University of Liverpool.

Cameron, E.N. & Desborough, G.A., 1964, Econ. Geol., 59, 197-225.

Cameron, W.E., McCulloch, M.T. & Walker, D.A., 1983, Earth Planet Sci. Lett., 65, 75-89.

Cameron, W.E., Nisbet, E.G. & Dietrich, V.J., 1979, Nature, 280, 550-53.

Campbell, I.H., 1978, Lithos, 11, 311-23.

Cann, J.R., 1970, Nature, Lond., 226, 928-30.

Cann, J.R., 1971, Geophys. J. Royal Astr. Soc., 39, 169-87.

Casey, J.F. & Karson, J.A., 1981, Nature, Lond., 292, 295-301.

Cassard, D. *et al.*, 1981, Econ. geol., 76, 805-831.

Chidester, A.H., 1962, US. Geol. Surv. Prof. Pap., pp 345

Chidester, A.H., 1968, In Studies in Appalachian geology (ed. Zen, White, Hadley), Northern and Maritime.

Chidester, A.H. & Cady, W.M., 1972, Nature, London, 240, 27-31.

Christensen, N.I. & Salisbury, M.H., 1979, J. Geophys. Res., 84, 4601-10.

Church, W.R. & Riccio, L., 1977, Can. J. Earth Sci., 14, 1156-65.

Church, W.R. & Stevens, R.K., 1971, J. Geophys. Res., 76, 1460-6.

Clarke, D.B., 1970, Contrib. Mineral. Petrol., 25, 203-224.

Clarke, D.B. & Pederson, A.K., 1976, In Geology of Greenland (ed. Escher, A. Watt, W.S.), Geol. Surv. Greenland, Copenhagen, 365-85.

Clarke, D.B. & Upton, B.G.J., 1971, Can. J. Earth Sci., 8, 248-58.

Cliff, R.A., 1985, J. geol. Soc. Lond., 142, 1, 97-110.

Cogger, N., 1980, Rep. 112, anal. chem. Unit., BGS.

Coish, R.A., 1977, Contrib. Mineral. Petrol., 60, 255-70.

Coish, R.A., Roden, M., Frey, F. & Suen, C.J., 1979, Geol. Soc. Am. Abstr. Prog., 11 (7), 403.

Coish, R.A., Hickey, R. & Frey, F.A., 1982, Geochim. Cosmochim. Acta., 46, 2117-2134.

Coleman, R.G., 1971, Geol. soc. Am. Bull., 82, 897-918.

Coleman, R.G., 1977, Ophiolites. Springer-Verlag, New York, 229 pp.

Coleman, R.G. & Donato, M.M., 1979, In Trondjemites (ed. Baker, F.) Elsevier.

Coleman, R.G. & Peterman, Z.E., 1975, J. Geophys. Res., 80, 1099-1108.

Cooper, A.F., 1976, NZ. J. Geol. Geophys., 19, 603-23.

Cox, K.G. *et al.*, 1979, The Interpretation of Igneous Rocks, George Allen & Unwin, London.

Crawford, R.G. & Davies, G., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.), George Allen & Unwin, London.

Crawford, A.J., Beccaluva, L. & Serri, G., 1981, Earth Planet Sci. Lett., 54, 346-56.

Crawford, A.J. & Cameron, W.E., 1985, Contrib. Mineral. Petrol., 91, 93-104.

Cullers, R.L. & Graf, J.L., 1984, In Rare earth element geochemistry (ed. Henderson, P.) Amsterdam, Elsevier.

Curtis, C.D. & Brown, P.E., 1969, Contrib. Mineral. Petrol., 24, 275-92.

Curtis, C.D. & Brown, P.E., 1971, Contrib. Mineral. Petrol., 31, 87-93.

Curtis, C.D., Brown, P.E. & Somogyi, V.A., 1969, Clay Minerals Bull., 8, 15-19.

Dalrymple, G.B., 1979, Geology, 7, 558-560.

Dalrymple, G.B. & Lanphere, M.A., 1971, Earth Planet Sci. Lett., 12, 300-8.

Dalrymple, G.B. & Lanphere, M.A., 1974, Geochim. Cosmochim. Acta., 38, 715-738.

Dalziel, I.W.D., *et al.*, 1974, Nature, London, 250, 291-4.

Deer, W.A. *et al.*, 1962, Rock forming minerals, Vols. 1-5, Longmans, London.

Davies, F.B. & Watson, J.V., 1977 J. geol. Soc. Lond., 133, 123-32.

Davies, H.L., 1971, Aust. Bur. Miner. Resour. Bull., 128.

Dempster, T.J., 1985, J. geol. Soc. Lond., 142, 1, 111-28.

Den Tex, E., 1969, Tectonophysics, 7, 457-488.

Dewey, J.F. & Pankhurst, R.J., 1970, Trans. R. Soc. Edinb., 68, 361-389.

Dewey, J.F. & Kidd, S.F., 1977, Bull. geol. Soc. Am., 88, 960-8.

Dewey, J.F. & Shackleton, R.M., 1984, Nature, 312, 115-21.

Dick, H.J.B., 1977, Am. J. Sci., 277, 768-800.

Dick, H.J.B., 1978, Geol. soc. Am., Abstr. Prog., 10, 38.

Dick, H.J.B. & Sinton, J.M., 1979, J. Geol., 87, 403-16.

Dick, H.J.B. & Fisher, R.L., 1983, Terra Cognita, 2, 242.

Dickey, J.S. *et al.*, 1979, In Origin and Distribution of the Elements (ed. Ahrens, L.H.), Pergamon Press, 587-95.

Dietrich, V.J., Emmerman, R. Oberhansli, R. & Puchelt, H., 1978, Earth Planet. Sci. Lett., 39, 127-44.

Dodson, M.H., 1984, Closure profiles in minerals, unpub.

Donaldson, C.H., 1974, Bull. geol. Soc. Am., 85, 1721-26.

Donaldson, C.H., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.), George Allen & Unwin, London.

Dostal, J. & Muecke, G.K., 1978, Earth Planet. Sci. Lett., 40, 415-22.

Downie, C. *et al.*, 1971, Inst. geol. Sci. Rep., No. 71/9, pp. 29.

Dowie, C., 1975, In A Correlation of Pre Cambrian Rocks in the British Isles. (ed. Harris, A.L. *et al.*,), Geol. Soc. spec. pub., 6, 113-115.

Drever, H.I. & Johnston, R., 1967, In Ultramafic and Related Rocks (ed. Wyllie, P.J.), John Wiley, New York.

Duffield, J. & Gilmore, G.R., 1979, J. Radioanalyt. Chem., 48, 135-45.

Dungan, M.A. & Ave-Lallement, H.G., 1977, In Magma Genesis (ed. Dick, H.J.B.) Ore Dept., Geol. Soc. India Bull., 96, 109-128.

Echeverria, L.M., 1980, Contrib. Mineral. Petrol., 73, 253-266.

Echeverria, L.M., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.), George Allen & Unwin, London.

Echeverria, L.M. & Aitken, B.G., 1986, Contrib. Mineral. Peterol., 92, 428-36.

Elliott, R.B., 1973, Contrib. Mineral. Petrol., 38, 71-79.

Elthon, D., 1979, Nature, Lond., 278, 514-8.

Elthon, D. & Casey, J.F., 1985, Geochim. Cosmochim. Acta., 49, 289-98.

Ferry, J.M. & Spears, F.S., 1978, Contrib. Mineral. Petrol., 66, 113-117.

Fitch, J.F. *et al.*, 1969, Geol. Soc. spec. pub., 3, 157-195.

Fitch, J.G. *et al.*, 1984, J. geol. Soc. Lond., 141, 1, 21-26.

Fisher, R.V., 1984, In (ed. Kokelaar, B.P. & Howells, M.F.), Geol. Soc. spec. pub.

Flinn, D., 1952, Geol. Mag., 89, 263-72.

Flinn, D., 1958, J. geol. Soc. Lond., 114, 107-36.

Fl;inn, D., 1956, J. Geol., 64, 480-505.

Flinn, D., 1967, Geol. J., 5, 251-90.

Flinn, D., 1970, Proc. geol. Ass., 81, 509-27.

flinn, D. *et al.*, 1972, Scot. J. Geol., 8, 335-43.

Flinn, D. & Pringle, I.R., 1976, Nature, London, 259, 299-300.

Flinn, D. Frank, P.L., Brook, M. & Pringle, I.R., 1979, In The Caledonides of the British Isles - reviewed (eds. Harris, A.L. *et al.*,), Geol. Soc. spec. pub., 8.

Flinn, D., 1985, In the Caledonide Orogen - Scandinavia and Related Areas (ed. Gee, D.G. & Sturt, B.A.), John Wiley & Son, Ltd., London.

Floyd, P.A., 1976, J. Petrol., 17, 522-545.

Floyd, P.A. & Winchester, J.A., 1975, Earth Plant. Sic. Lett., 27, 211-218.

Frank, P., 1977, unpub. Ph.D. Thesis, University of Liverpool.

Ford, C.E. *et al.*, 1983, J. Petrol., 24, 256-65.

Fountain, D.M. & Salisbury, M.H., 1981, Earth Planet. Sci. Lett., 56, 263-77.

Fowler, M.B., Williams, H.R. & Windley, B.F., 1981, Min. Mag., 44, 171-7.

Fowler, M.B., Williams, C.T. & Henderson, P., 1983, Min. Mag., 47, 547-53.

Francis, G.H., 1956, Am. J. Sci., 254, 201-226.

Francis, D., 1985, contrib. Mineral. Petrol., 89, 144-54.

Frey, F.A., 1969, Geochim. Cosmochim. Acta., 33, 1429-1447.

Frey, F.A., 1970, Phys. Earth Planet. Inter., 3, 323-30.

Frey, F.A., 1970, Earth Planet. Sci. Lett., 7, 351-360.

Frey, F.A., 1984, In Rare earth element geochemistsry (ed. Henderson, P.), Elsevier, 153.

Frey, F.A., Haskin, L.A. & Haskin, M.A., M.A., 1971, J. Geophys. Res., 75, 2057-2070.

Frey, F.A., Green, D.H. & Roy, S.D., 1978, J. Petrol., 19, 463-513.

Frey, F.A., Suen, C.J. & Stockman, H.W., 1985, Geochim, Cosmochim. Acta., 49, 2469.

Frey, F.A. *et al.*, 1981, Abstr. Am. Geophys. Union.

Fujii, T. & Scarfe, C.M., 1985, Contrib. Mineral. Petrol., 90, 18-28.

Furnes, H. *et al.*, 1985, In The Caledonides Orogen - Scandinavia and Related areas. (ed. Gee, D.G. & Stunt, B.A.) John Wiley & Sons Ltd., London.

Garmann, L.B., Brunfeldt, A.O., Finstad, K.G. & Heier, K.S., 1975, Chem. Geol., 15, 103-116.

Garson, M.S. & Plant, J.A., 1973, Nature Phys. Sci., 242, 34-38.

Gass, I.G., Neary, C.R., Pritchard, H.M. & Bartholomew, I.D., 1982, Report of the E.E.C. raw materials project, 263 pp.

Gass, I.G. & Smewing, J.D., 1973, Nature, Lond., 242, 26-9.

Glennie, K.W., Boeuf, M.G.A., Hughes-Clack, M.W.H., Moody-SAtuart, M., Pilaar, W.F.H., Rheinhardt, B.M., 1974, Koninkl. Ned. Geol. Mijnbouw. Genoot. Verh., 31.

Gill, K.R., 1965, unpub. Ph.D. Thesis, University of Cambridge.

Giraradeau, J. & Nicolas, A., 1981, Tectonophys., 77, 1-34.

Goldman, D.S. & Albee, A.L., 1977, Am. J. Sci., 277, 750-767.

Graham, C.M., 1976, J. geol. Soc. Lond., 132, 61-84.

Graham, C.M. & Bradbury, H.J., 1981, Geol. Mag., 118, 27-37.

Graham, C.M. & England, P.C., 1976, Earth Planet. Sci. Lett., 31, 142-52.

Green, D.H., 1967, In Ultramafic and related rocks (ed. Wiley, P.J.), John Wiley & Sons, Inc., New York.

Green, D.H. & Ringwood, A.E., 1967, Contrib. Mineral. Petrol., 15, 103.

Green, D.H., Hibberson, W.O. & Jacques, A.L., 1979, In The Earth: Its Origin, Structure and Evolution (ed. McElhinny, M.W.), Academic Press, 265.

Grove, T.L. & Bryan, W.B., 1983, Contrib. Mineral. Petrol., 84, 293-309.

Hajash, A., 1984, contrib. Mineral. Petrol., 84, 409-12.

Harland, W.B., Cox, A.V., Llewellyn, P.G., Pickton, C.A.G., Smith, A.G. & Walters, R., 1982, A Geological Time Scale, Camb. Univ. Press, Cambridge.

Harper, C.T., 1967, Earth Planet. Sci. Lett., 3, 128-32.

Harris, A.L. & Pitcher, W.S., 1975, In A Correlation of Precambrian Rocks in the British Isles. (ed. Harris, A.L. *et al.*) Geol. soc. spec. pub., 6, 52-75.

Harris, A.L. *et al.*, 1978, In Crustal Evolution in NW Britain and Adjacent Regions (ed. Bowes, D.R. & Leake, B.E.), Geol. J. Spec. Issue No. 10, 115-138.

Harrison, T.M., 1981, Contrib. Mineral. Petrol., 78, 324-331.

Harrison, T.M., 1983, Isotope Geoscience, 1, 319-338.

Harrison, T.M. & McDougall, I. 1981, Earth Planet. Sci. Lett., 55, 123-49.

Harrison, T.M. & McDougall, I., 1980, Geochim. Cosmochim. Acta., 44, 2004-20.

Harte, B., 1977, J. Geol., 85, 279-288.

Harte B., 1982, In Continental Basalts and Mantle Xenoliths (ed. Hawkesworth, C.J. & Norry, M.J.), Shiva, Nantwick.

Haskin, L.A., Frey, F.A., Schmitt, R.A. & Smith, R.H., 1966, Phy. Chem. Earth, 7, 67-3231.

Haskin, L.A. & Korotex, R.L., 1977, Geochim. Cosmochim. Acta., 41, 921-39.

Haskin, L.A. & Haskin, M.A., 1968, In Origin and Distribution of the Elements (ed. Arhens, L.H.), Pergamon, New York.

Hawkesworth, C.J. & O'Nions, R.K., 1977, J. Peterol., 18, 487-520.

Hawkesworth, C.J. *et al.*, 1977, Earth Planet. Sci. Lett., 36, 253-62.

Hawkins, w., 1980, In Ophiolites (ed. Panayiotou, A.) Geol. Survey Dept., Cyprus.

Heddle, M.F., 1878, The County Geognosy and Mineralogy of Scotland, Orkney & Shetland, Truro.

Heddle, M.F., 1879, Min. Mag., 2, 12-35; 106-33; 155-90; 253-5.

Hellman, P.L., Smith, R.E. & Henderson, P., 1979, Contrib. Mineral. Petrol., 71, 23-44.

Henderson, P., 1984, Rare earth element geochemistry, Elsevier, Amsterdam.

Henderson, W.G. & Robertson, A.H.F., 1982, J. geol. Soc. Lond., 139, 4, 433-50.

Herrmann, A.G., Potts, M.J. & Knake, D., 1974, Contrib. Mineral. Petrol., 44, 1-16.

Herrmann, A.G. *et al.*, 1976, Contrib. Mineral. Peterol., 59, 1-12.

Hess, H.H. *et al.*, 1952, Econ. Geol., 28, 634-675.

Hibbert, S. 1819-20, Edin. Phil. Int., 1, 296-314; 2, 67-79, 224-42.

Hibbert, S. 1822. A Description of the Shetland Isles. Edinburgh.

Hickey, R. & Frey, F.A., 1982, Geochim. Cosmochim. Acta., 46, 2099-2115.

Himelberg, G.R. & Loney, R.A., 1973, Geol. Soc. Am. Bull., 84, 1585-1600.

Hitchen, C.S., 1929, Mining Mag. Lond., 40, 18-24.

Holm, P.E., 1982, Contrib. Mineral. Petrol., 79, 308-10.

Hopson, C.A. & Pallister, J.S., 1980, In Ophiolites (ed. Panayiotou, A.), Geol. Survey Dept.

Hsu, K.J., 1969, Geol. Soc. Am. Bull., 180, 927-52.

Hubbert, M.K. & Rubey, W.W., 1959, Geol. soc. Am. Bull., 70, 115-66.

Humphris, S.E., 1984, In Rare earth element geochemistry (ed. Hendedrson, P.), Amsterdam, Elsevier.

Humphris, S.E. & Thompson, G., 1978, Geochim. Cosmochim. Acta., 42, 127-36.

Humphris, S.E., Morrison, M.A. & Thompson, R.N., 1978, Chem. Geol., 23, 125-137.

Huppert, H.E., Sparks, R.S.J., Turner, J.S. & Arndt, N.T., 1984, Nature, 309, 19-22.

Huneke, J.C. & Smith, S.P., 1976, Proc. 7th Lunar Sci. Conf., 1987-2008.

Hutton, D.A.W., Aftalion, M. & Halliday, A.N., 1985, Nature, 315, 210-12.

Hynes, A., 1980, Contrib. Mineral. Petrol., 75, 79-87.

Idlefonse, J.P. & Gabis, V., 1976, Geochim. Cosmochim. Acta., 40, 297.

Irvine, T.N., 1963, Min. Soc. Am. Spec., Paper 1, 36-45.

Irvine, T.N., 1967, In Ultramafic and related rocks (ed. Wyllie, P.J.), John Wiley & sons, Inc., New York.

Irvine, T.N., 1974, Geol. Soc. Am. Mem., 138.

Irvine, T.N., 1976, Geol. survey of Canada paper, 76 - 1A, 76-81.

Irvine, T.N., 1980, In Physics of Magmatic Processes (ed. Hargraves, R.B.), Princeton Univ. Press, Princeton, U.S.A.

Irvine, T.N., 1982, J. Petrol., 23, 127-62.

Irvine, T.N. & Baragar, W.R.A., 1971, Can. J. Earth Sci., 8, 523-48.

Irvine, T.N. & Findlay, D.C., 1972, In The Ancient Oceanic Lithosphere (ed. Irving, E.), Earth Physics Rev. Publ., 42, 97-126.

Irvine, T.N. & Smith, C.H., 1967, In Ultramafic and related rocks (ed. Wyllie, P.J.), John Wiley & sons, Inc., New York.

Irving, A.J., 1978, Geochim. Cosmochim. Acta., 42, 743-770.

Jackson, E.D., 1967, In Ultramafic and related rocks (ed. Wyllie, P.J.), John Wiley & Sons, Inc., New York.

Jackson, E.D. & Thayer, T.P., 1972, 24th Int. Geol. Congr. Montreal, Sect. 2, 289-296.

Jacobsen, S.B. & Wasserburg, G.J., 1979, J. Geophys. Res., 84, 7429-45.

Jacques, A.L., 1981, J. Petrol., 22, 1-40.

Jacques, A.L. & Chappell, B.W., 1980, Contrib. Mineral. Petrol., 75, 55-70.

Jacques, A.L., Chappell, B.W. & Taylor, S.R., 1983, Contrib. Mineral. Petrol., 82, 154-64.

Jager, E., 1979, In Lectures in Isotope Geology (ed. Jager, E. & Hunzikier, J.C.), Springer-Verlag, Berlin.

Jahns, R.H., 1967, In Ultramafic and Related Rocks (ed. Wyllie, P.J.), John Wiley & Sons, Inc., New York.

Jahn, B.-M., 1986, Contrib. Mineral. Petrol., 92, 195-206.

Jahn, B.-M., Auvray, B., Blais, S., Capdevila, R., Cornichet, J., Vidal, F. & Hameurt, J., 1980, J. Petrol., 21, 201-44.

Jahn, B.-M., Grau, G. & Glickson, A.Y., 1982, Contrib. Mineral. Petrol., 80, 25-40.

Jameson, R., 1978, An outline of the mineralogy of the Shetland Islands and of Arran. Edinburgh.

Jameson, R., 1800, Mineralogy of the Scottish Isles, Edinburgh, Vol. 2, 185-224.

Jamieson, R.A., 1981, J. Petrol., 22, 397-449.

Jelinek, E., Soucek, J., Randa, Z., Jakes, P., Bluck, B.J. & Bowes, D.R., 1984, Trans. R. Soc. Edin. Earth Sci., 75, 193-209.

Jenner, G.A., 1981, Chem. Geol., 33, 307-32.

Jibiki, H. & Masuda, A., 1974, Mar. Geol., 16, 205-211.

Kay, R.W. & Senechal, R.G., 1976, J. Geophys. Res., 81, 964-70.

Keleman, P.B. & Ghiorso, M.S., 1986, Contrib. Mineral. Petrol., 94, 12-28.

Kidd, W.S.F., 1977, Geophy. J. R. Astro. Soc., 50, 149-183.

Kokelaar, P., 1986, Bull. Volcanol., 48, 275-89.

Koons, R.O., 1981, Contrib. Mineral. Petrol., 78, 189-95.

Korzhinsky, D.S., 1970, Theory of Metasomatic Zoning, Oxford Univ. Press, London.

Krishnamurthy, P. & Cox, K.G., 1977, Contrib. Mineral. Petrol., 62, 53-75.

Kuno, H., 1967, In Basalts (ed. Hess. H. & Poldervaart, A.), Interscience, New York, 623-688.

Kuo, H. Y. & Crocket, J.H., 1979, Econ. Geol., 74, 590-605.

Kushiro, I., 1969, Am. J. Sci. 267A, 269-294.

Langmuir, C.H. & Hanson, G.N., 1980, Phil. Trans. R. Soc. Lond., A297, 383-408.

Leake, B.E., 1978, Can. Mineral., 16, 501-20.

Leake, B.E., 1982, In Igneous rocks of the British Isles (ed. Sutherland, D.S.), John Wiley & Sons, Chichester.

Leeman, W.P., 1974, unpub. Ph.D. Thesis, University of Oregon.

Le Roex, A., Erlank, A.J. & Needham, H.D., 1981, Contrib. Mineral. Petrol., 77, 24-37.

Lofgren, G.E. & Donaldson, C.H., 1975, Trans. Am. Geophys. Union, 56, 468.

Longhi, J. *et al.*, 1978, Geochim. cosmochim. Acta., 42, 1545-1558.

Lopez-Escobar, L. *et al.*,1979, Contrib. Mineral. Petrol., 70, 439-50.

Loubet, M. & Allegre, C.J., 1979, Geochem. J., 13, 69-75.

Loubet, M., Shimizu, N. & Allegre, C.J., 1975, Contrib. Mineral. Petrol., 58, 1-12.

Loubet, M., Bougault, M., Shimizu, N. & Allegre, C.J., 1976, EOS., 57, 1025.

Loubet, M., Polve, M., Richard, P. & Allegre, C.J., 1980, Colloq. Inst. C.N.R.S., 272, 269.

Loughman, F.C., 1969, Chemical Weathering of the Silicate Minerals, Elsevier, New York.

MacDonald, G.A. & Katsura, T., 1964, J. Petrol., 5 (1), 82-133.

Macgregor *et al.*, 1940, Mem. geol. Surv. Gt. Brit. Min. Resources, 33.

MacRae, N.D., 1969, Can. J. Earth Sci., 6 (2), 281-303.

Malpas, J., 1979, Can. J. Earth Sci., 16, 2086-101.

Maltman, A.J., 1978, Geol. Soc. Am. Bull., 89, 972-80.

Masuda, A., Nakamura, N. & Tanaka, T., 1973, Geochim. Cosmochim. Acta., 37, 239-48.

McBinney, A.R. & Noyes, R.M., 1979, J. Petrol., 20, 487-554.

McCulloch, M.T. & Cameron, W.E., 1983, Geology, 11, 727-731.

McQuillin, R. & Brooks, M., 1967, Geophys. Pap. No. 2, B.G.S., 1-22.

Menzies, M., 1976, Geochim. Cosmochim. Acta, 40, 645-56.

Menzies, M. & Allen, C.A., 1974, Contrib. Mineral. Petrol. 45, 197-213.

Menzies *et al.*, 1977, Geochim. Cosmochim. Acta., 41, 1419-30.

Menzies *et al.*, 1977, Contrib. Mineral. Peterol., 64, 53-74.

Menzies, F.M., Blanchard, D. & Jacobs, J., 1977, Earth Planet. Sci. Lett., 37, 203-15.

Meschede, M., 1986, Chem. Geol., 56, 207-18.

Miller, J.A. & Flinn, D., 1966, Geol. J., 5, 95-116.

Miyashiro, A., 1975, J. Geol., 83/2, 249-81.

Moller, P. & Muecke, G.K., 1984, Contrib. Mineral. Petrol., 87, 242-50.

Montigny, R., Bougault, H., Botting, Y. & Allegre, C.J., 1973, Geochim. Cosmochim. Acta., 37, 2135-2147.

Moody, J.B., 1976, Lithos, 9, 125-38.

Moores, E.M., 1969, Geol. Soc. Am. Spec. Paper, 118, 1-74.

Moores, E.M., 1982, Rev. geophys. Space Phys., 20, 735-60.

Moores, E.M. & Vine, F.J., 1971, Phil. Trans. R. Soc. Lond., A268, 443-66.

Morrison, M.A., 1978, Earth Planet. Sci. Lett., 39, 407-16.

Murase, T. & McBirney, A.R., 1973, Geol. Soc. Am. Bull., 84, 3563-592.

Mussett, A.E., 1969, Geophys. J.R. Astro Soc., 18, 257-303.

Mussett, A.E., Ross, J.G. & Gibson, I.L., 1980, Geophys. J.R. Astro. Soc., 60, 37-52.

Mykura, W. & Phemister, J., 1976, Mem. geol. Surv. Gt. Br.

Mykura, W. & Young, B.R., 1969, Rep. B.G.S., No. 69/4.

Naldrett, A.J. & Campbell, I.H., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.) George Allen & Unwin, London.

Nesbitt, R.W., 1971, Sp. Publ. Geol. Soc. Aust., 3, 331-47.

Nicolas, A. & Jackson, E.D., 1972, Schweiz. Mineral. Petrogr. Mitt., 52, 479-95.

Nicolas, A. Jackson, 1982, J. Petrol., 33, 568.

Nisbet, E.G., Bickle, M.J. & Martin, A., 1977, J. Petrol., 18, 521-66.

Nisbet, E.G., Bickle, M.J., Martin, A., Orpen, J.L. & Wilson, J.F., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.) George Allen & Unwin, London.

Nockolds, S.R., 1941, J. geol. Soc. Lond., 96, 451-511.

Noiret, G., Montigny, R. & Allegre, C.J., 1981, Earth Planet. Sci. Lett., 56, 375-86.

Obata, M., 1980, J. Petrol., 21, 533-572.

Obata, M., Suen, C.J. & Dicken, J.S., 1980, Colloq. Int. C.N.R.S., 272, 257-268.

O'Hara, M.J., 1968, Earth Sci. Rev., 4, 69-133.

O'Hara, M.J., 1977, Nature, 266, 503-7.

O'Hara, M.J. & Matthews, R.E., 1981, J. geol. Soc. Lond., 138, 237-77.

Ottonello, G., Piccardo, G.B. & Enst, W.G., 1979, Geochim. Acta., 43, 1273.

Ottonello, G., Enst, W.G. & Joron, J.L., 1984, J. Petrol., 25, 343-72.

Ottonello, G., Joron, J.L. & Piccardo, G.B., 1984, J. Petrol., 25, 373-93.

O'nions, R.K. & Clarke, D.B., 1972, Earth Planet. Sci. Lett., 15, 436-446.

Pallister, J.S., 1981, J. Geophys. Res., 86.

Pallister, J.S., 1984, In Ophiolites (ed. Gass *et al.*), Geol. Soc. spec. pub., 13.

Pallister, J.S. & Hopson, C.A., 1981, J. Geophys. Res., 86, 2593-644.

Pallister, J.S. & Knight, R.J., 1981, J. Geophys. Res., 86, 2673-2697.

Pankhurst, R.J. *et al.*, 1982, In Igneous Rocks of the British Isles (ed. Sutherland, D.S.), John Wiley & Sons, Ltd., Chichester.

Paster, T.P. *et al.*, 1974, Geochim. Cosmochim. Acta., 38, 1549-1577.

Pearce, J.A., 1975, Tectonophysics, 25, 41-67.

Pearce, J.A., 1980, In Ophiolites (ed. Panayiuotou, A.), Geol. Survey Dept., Cyprus.

Pearce, J.A. & Cann, J.R., 1971, Earth Planet. Sci. Lett., 12, 339-349.

Pearce, J.A. & Cann, J.R., 1973, Earath Planet. Sci. Lett., 19, 290-300.

Pearce, J.A. & Norry, M.J., 1979, Contrib. Mineral. Petrol., 69, 33-47.

Pearce, J.A. *et al.*, 1981, Phil. Trans. R. Soc. London, A300, 299-317.

Pearce, J.A. *et al.*, 1984. In (ed. Kokelaar, B.P. & Howells, M.F.), Geol. Soc. spec. pub.

Penchuk, L.L., 1970, Geochim. Int., 7, 157-179.

Phemister, J., 1964, Advancing Frontiers in Geology and Geophysics, 279-95.

Phemister, J., 1979, The ORS intrusive complex in northern Northmaven, B.G.S., Ref. 78/2, OHMS.

Phillips, A.H. & Hess, H.H., 1936, Am. Min., 21, 333-362.

Phillips, F.C., 1927, J. geol. Soc. Lond., 83, 622-51.

Phillips, F.C., 1928, Geol. Mag., 63, 72-7.

Philpotts, J.A. *et al.*, 1972, Geochim. Cosmochim. Acta., 36, 1136-1166.

Piper, J.D.A., 1982, Earth Planet. Sci. Lett., 59, 61-89.

Pitcher, W.S. & Berger, A.R., 1972, The Geology of Donegal: A study of Granite Emplacement and Unroofing, Wiley Int., New York.

Plant, J. *et al.*, 1975, Br. Orogens 5th Trienn. Symp., BGS.

Potts, M.J. & Condie, K.C., 1971, Contrib. Mineral. Petrol., 33, 245-258.

Prestvik, T., 1980, In Ophiolites (ed. Panayiotou, A.), Geol. Survey Dept., Cyprus.

Pringle, I.R., 1970, Geol. J., 7, 147-70.

Pritchard, H., 1985, In (ed. Gee, D.G. & Sturt, B.A.), John Wiley & Sons, Ltd.

Pritchard, H. & Neary, C.R., 1981, In An Int. Symp. Metal. Mafic and Ultramafic Complexes, UNESCO. Pub., Athens.

Pritchard, H. & Neary, C.R., 1982, Ofioliti, 2/3, p 455-466.

Pritchard, H. *et al.*, 1981, Trans. Inst. Min. Metall., 90, B186-188.

Prinzhofer, A. *et al.*, 1980, Tectonophysics, 69, 85.

Prinzhofer, A. & Allegre, C.J., 1985, Earth Planet. Sci. Lett., 74, 251-65.

Pyke, D.R. *et al.*, 1973, Geol. Soc. Am. Bull., 84, 955-78.

Quick, J..E., 1981, J. Geophys. Res., 86, 11837-11863.

Raedeke, L.D. & McCallum, I.S., 1983, J. Petrol., 25, 2, 395-420.

Rathbone, P.A. & Harris, A.L., 1979, In Caledonides of the British Isles (ed. Harris, A.L., Holland, C. & Leake, B.E.), Geol. Soc. spec. pub., 8, 101-107.

Read, H.H., 1934, Min. Mag., 23, 519-40.

Read, H.H., 1934, J. geol. Soc. Lond., 90, 637-88.

Rread, H.H., 1936, Proc. Geol. Ass., 47, 283-93.

Rread, H.H., 1937, Trans. R. Soc., Edinb., 59, 195-221.

Reed, S.J.B., 1975, Electron Microprobe Analysis, Cambridge Univ. Press.

Ries, A.C., Shackleton, R.M., Graham, R.H. & Fitches, W.R., 1983, J. geol. Soc. Lond., 140, 75.

Rivington, J.B., 1953, Min. Mag. London, 89, 329-37.

Robertson, A.H.F. & Henderson, W.G., 1984, Trans. R. Soc. Edin. Earth Sci., 75, 135-50.

Robinson, T., 1983, unpub. Ph.d. Thesis, University of Liverpool.

Rocci, G. *et al.*, 1975, Petrologie, 1, 172-4.

Rock, N.M.S., Jeffreys, L.A. & Macdonald, R., 1984, Scott. J. Geol., 20, 383-406.

Rock, N.M.S., Macdonald, R., Szucs, Bower, 1982, Scott. J. Geol., 22, 107-26.

Roeder, P.L. & Emslie, R.F., 1970, Contrib. Mineral. Petrol., 29, 275-89.

Rogers, M., Allen, R., Nagle, C. & Fitzhugh, W., 1983, Archaeometry, 25 (2), 186.

Rothery, D.A., 1983, J. geol. Soc. Lond., 140, 287.

Sabine, P., 1978, Geol. Mag., 115, 463-466.

Sandison, C.G.D., 1948, Scott. Council. (Dev. and Ind.), 49 (1).

Savage, D., 1979, unpub. Ph.D. Thesis, London Imperial College.

Saunders, A.D. *et al.*, 1979, Bull. geol. Soc. Am., 90, 237-258.

Sanders, A.D. *et al.*, 1980, in Ophiolites (ed. Panayiotou, A.), Geol. Survey Dept., cyprus.

Saunders, A.D., 1984, In Rare earth element geochemistry (ed. Henderson, P.), Elsevier.

Saunders, A.D. & Tarney, J., 1984. In (ed. Kokelaar, P.B. & Howells, M.F.) Geol. Soc. spec. pub.

Schiffries, C.M., 1982, Econ. Geol., 77, 1439-53.

Schilling, J.-G., 1973, Nature, 242, 565-71.

Schilling, J.-G., 1975, Eearth Planet. Sci. Lett., 125, 102-115.

Schilling, J.-G. & Winchester, J., 1969, Contrib. Mineral. Petrol., 23, 27-37.

Schilling, J.-G. *et al.*, 1976, Nature, 26, 108-113.

Scottish Council (Dev. and Ind.), 1954, Rep. Min. Res. Panel. on Serpentine and Olivine-rock in Scotland.

Sharaskin, A.Y. *et al.*, 1983, Ofioliti, 8 (3), 411-30.

Sharaskin, A.Y. *et al.*, 1983, Ofioliti, 8 (3), 431-38.

Shih, C.Y., 1972, unpub. Ph.D. thesis, Columbia University, New York.

Searle, M.P. & Malpas, J., 1980. Trans. R. Soc. Edinb.

Shih, C.Y. & Gast, P.W., 1971, Abstr. Prog. Annu. Meet. Geol. Soc. Am., 3 (7), 702.

Size, W.B., 1985, In (ed. Gee, D.G. & Sturt, B.A.), John Wiley & Sons Ltd., Chichester.

Smith, R.E. & Smith, S.E., 1976, Earth Planet. Sci. Lett., 32, 114-20.

Smewing, J., 1981, J. Geophys. Res., 86, 2645-2659.

Snoke, A.W. *et al.*, 1981 J. Petrol., 22, 501-52.

Snoke, A.W. *et al.*, 1982, Geology, 10, 160-66.

Soper, N.J. & Barber, A.J., 1982, J. geol. Soc. Lond., 139, 127-38.

Sinton, J., 1979, Contrib. Mineral. Petrol., 70, 49-57.

Sparks, R.S.J. *et al.*, 1984, Phil. Tran. R. Soc. Lond., A310, 511-34.

Selfridge, G.C., 1936, Am. Min., 21, 463-501.

Spray, J.G., 1984, In Ophiolites & Oceanic Lithosphere (ed. Gass *et al.*,), Geol. Soc. spec. pub., 13.

S.-Seymour, K. *et al.*, 1983, Contrib. Mineral. Peterol., 84, 6-14.

Stillman, C.J. & Williams, C.J., 1978, Earth Planet. Sci. Lett., 41, 288-310.

Stern, C.R. & Elthon, D., 1979, Tectonophysics, 55, 179-213.

Steiger, R.H. & Jager, e., !(&&, Earth Planet. Sci. Lett., 36, 359-62.

Stern, C.R., 1980, J. Geophys. Res., 85, 955-66.

Stephens, M..B., 1980, Norges geol. unders., 360, 159-93.

Streckeisen , A., 1976, Earth Sci. Rev., 12, 1-33.

Streckeisen, A., 1979, Geology, 7, 331-35.

Strong, D.F. & Malpas, J., 1975, Can. J. Earth Sci., 12, 894-896.

Sturt, B.A. *et al.*, 1980, Norges geol. und., 358, 1-30.

Suen, C.J., Frey, F.A. & Malpas, J., 1979, Earth Planet. Sci. Lett., 45, 337-48.

Sun, S.S. & Nesbitt, R.W., 1977, Earth Planet. Sci. Lett., 35, 429-48.

Sun, S.S., & Nesbitt, R.W., 1978, Contrib. Mineral. Peterol., 65, 301-25.

Sun, S.S. & Nesbitt, R.W., 1978, Geology, 6, 689-93.

Sun, S.S., Nesbitt, R.W. & Sharaskin, A.Y., 1979, Earth Planet. Sci. Lett., 44, 119-38.

Sutherland, D.S, 1982, Igneous Rocks of the British Isles, John Wiley & Sons Ltd., Chichester.

Tait, S.R. *et al.*, 1984, Lithos, 17 (2), 139-46.

Takahashi, E. & Scarfe, C.M., 1985, Nature, 315, 566-68.

Taylor, G.K., 1984, unpub. Ph.D. Thesis, University of Liverpool.

Taylor, H.P., 1967, In Ultramafic and related rocks (ed. Wyllie, P.J.), John Wiley & Sons, Inc., New York.

Taylor, H.P. & Noble, J.A., 1960, 21st Intern. Geol. Congr., Copenhagen, Repts., 13, 175-187.

Thirlwell, M.F. & Bluck, B.J., 1984, In Ophiolites and Oceanic Lithosphere (ed. Gass, I.G., Lippard, S.J. & Shelton, A.W.), Geol. Soc. spec. pub., No. 13.

Thayer, T.P., 1960, 21st Intern. Geol. Congr., Copenhagen, Reports., 13, 247-259.

Thayer, T.P., 1967, In Ultramafic and related rocks (ed. Wyllie, P.J.), John Wiley & Sons. Inc., New York.

Thomas, C.H., 1980, Rep. 113, Anal. Chem. Unit, B.G.S.

Thompson, A.B., 1976, Am. J. Sci., 276, 425-54.

Thompson, G., 1973, Chem. Geol., 12, 99-111.

Thy, P., 1984, Ofioliti, 9 (3), 555-68.

Tual, E., Jahn, B.M., Bougault, H. & Joron, J.L., 1985, Init. Rept. DSDP., Washington DC, U.S. Govt. Printing Office, 83, 201-14.

Turner, G. 1968, In Origin and Distribution of the Elements (ed. Arhens, L.H.), Peregamon, Oxford, 30, 387-398.

Turner, F.J. & Verhoogen, J., 1960, Igneous and Metamorphic Petrology, 2nd ed. McGraw-Hill Book co., New York, 694pp.

Valance, T.G., 1965, Min. Mag., 34, 471-481.

Valance, T.G., 1969, Proc. Linn. Soc. NSW., 94, 8-53.

Viljoen, M.J. & Viljoen, R.P., 1969, Sp. Publ. Geol. Soc. S. Afr., 2, 55-85.

Viljoen, M.J., Viljoen, R.P. & Pearton, T.N., 1982, In Komatiites (ed. Arndt, N.T. & Nisbet, E.G.), George Allen & Unwin, London.

Wadsworth, W.J., 1982, In Igneous rocks of the British Isles (ed. Sutherland, D.S.), John Wiley & Sons, Inc., Chichester.

Wager, L.R. & Brown, G.M., 1968, Layered Igneous Rocks, Oliver and Boyd Ltd., Edinburgh.

Wager, L.R., Brown, G.M. & Wadsworth, W.J., 1960, J. Petrol., 1, 73-85.

Wager, L.R. & Dear, W.A., 1939, Medd. Groenl. 105, No. 4

Wanke, H., Baddenhausen, H., Spettel, B., Tesche, F., Quijano-Rico, M., Dreibus, G. & Palme, H., 1972, Meteoritics, 7, 579-89.

Watson, J.V., 1984, J. geol. Soc. Lond., 141, 2, 193-214.

Weaver, B.L. & Tarney, J., 1981, Contrib. Mineral. Petrol., 78, 175-88.

Whitford, D.J. & Arndt, N.T., 1977, Carnegie Inst. Washington, 76, 863-70.

Whitford, D.J. & Arndt, N.T., 1978, Earth Planet Sci. Lett., 41, 188-96.

Wicks, F.J. & Plant, A.G., 1979, Can. Mineral., 17, 785-830.

Wicks, F.J. & Whittaker, E.J.W., 1977, Can. Minerol., 15, 459-88.

Wicks, F.J., Whittaker, E.J.W. & Zussman, J., 1977, Can. Mineral., 15, 446-58.

Williams, W.A., 1977, unpub. Ph.D. Thesis, University of Virginia.

Wilkinson, J.F.G., 1953, Geol. Mag., 90, 305-21.

Wilkinson, J.F.G., 1974, In The Alkaline Rocks (ed. Sorensen, H.), Wiley - Int., New York, 67-95.

Windley, B.F., 1982, In Igneous rocks of the British Isles (ed. Sutherland, D.S.), John Wiley & Sons, Inc., Chichester.

Wilson, A.H., 1982, J. Petrol., 23, 2, 240-292.

Wilson, J.R., Esbensen, K.H. & Thy, P., 1981, J. Petrol., 22, 584-627.

Wilson, G..V. & Phemister, J., 1946, Geol. Surv. Gt. Br. Wartime Pamphlet, No. 9.

Wood, C.P., 1980, Nature, 288, 692.

Wood, D.A., Joron, J.-L., Treuil, M., Norry, M.J. & Tarney, J., 1979, Contrib. Mineral. Petrol., 70, 319-39.

Wood, D.A. *et al.*, 1976, Contrib. Mineral. Petrol., 55, 241-254.

Zimmerman, J.-C., 1972, Sci. Terre. Mem., 2, pp 188.