Geochronological and Petrological studies of the Thermal Evolution of the Dalradian, South West Scottish Highlands

by

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"I don't see much sense in that," said Rabbit.

"No," said Pooh, humbly, "there isn't. But there was going to be when I began it. It's just that something happened to it on the way."
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I declare that the results reported, and the thoughts and conjectures expressed and made, in this thesis are my own work, and the products of my own mind, unless otherwise acknowledged. I also declare that no part of this thesis has been submitted for any other degree or qualification.
Abstract

The Scottish Dalradian is lithologically diverse. This is because it has been divided into provinces of varying depositional, structural and metamorphic histories, by lineaments in the deep crust, inferred by observation of the geology, and observed by geophysical measurement. The South West Highlands is one of the larger of these provinces, and the most distinct; its tectonometamorphic evolution has been constructed in detail, and has been shown to be distinct because of the high proportion of mafic, and gneissic, rock that is present in the crust.

Deformation has occurred in two episodes. The first, and dominant, episode involved the nucleation, and propagation of recumbent isoclinal folds, as nappes, in deep levels of the crust. These folds nucleated in rheologically weak layers in the crust in the Dalradian sequence, and propagated by hinge-rolling with the region of the crust richest in rigid mafic rock undergoing the least pervasive deformation, and acting as a rheological and gravitational anchor for the two nappes. One of the nappes, the Islay Anticline, rides north-west ward over the West of Islay Shear Belt, while the other, the Tay Nappe, rides south-eastwards, but its base is not exposed. This deformation is correlated with the \( D_1-D_2 \) deformation of Harris et al. (1976) and Harte et al. (1984).

The secondary deformation is more restricted, but locally pervasive, and affects the deeper structural levels now exposed in Northern Kintyre, to the south-east. It occurred in at least two phases, the first being a hitherto unrecognised episode during which albite porphyroblasts grew. This episode, based on inclusion trail geometries in albite porphyroblasts, involved shearing and isoclinal folding, and is correlated with the \( D_3 \) deformation of Harris et al. (1976) and Harte et al. (1984). The later phase of secondary deformation involved monoformal folding and modification of the geometry of the \( D_1-D_2 \) structures. It resulted in the exposure of deeper structural levels in the core of the Cowal Antiform, and is correlated with the \( D_4 \) deformation in the Central and Southern Highlands.

Accompanying both phases of deformation was metamorphism. The primary
metamorphism resulted in the growth of the dominant biotite and garnet zone assemblages in the region, the low grades and early timing of growth of these assemblages relative to the deformational history being distinctive in the South West Highlands. The mineral assemblages in pelites are strongly dependent on bulk rock composition, as indicated by phengite chemistry which is also dependent on metamorphic grade. Phengites in biotite-chlorite-bearing assemblages become Al- and Mg-richer with increasing grade, but are Si- and Fe-richer than isogradic biotite-absent assemblages. Thus, biotite growth at a given grade is favoured by Fe- and Si-rich bulk rock compositions. Garnet growth is also favoured in Fe-rich bulk rock chemistries. The chemical changes recorded in garnet growth zoning, suggest that the primary metamorphism occurred while the rocks were heating. The resetting of garnet zoning in the highest grade primary assemblage studied suggests that the region remained at close to maximum temperatures for a long time, or that post-primary metamorphic cooling rates were slow. Simple correlations between grade and lithology and exposed structural depth suggest that the garnet zone is more extensive than hitherto thought; this is confirmed by the presence of almandine-grossular-rich garnet remnants in Northern Kintyre, previously assigned to the biotite zone.

The secondary metamorphism is restricted to rocks affected by secondary deformation, and also occurs in distinct stages. The earlier stages are best developed in oxidised schists exposed in Northern Kintyre. The oxidising conditions resulted in the growth and stability of Mn-rich garnet, coexisting with chlorite, while biotite remained unstable. The marked difference in rock bulk chemistry, and the presence of overprinting metamorphic assemblages has resulted to mis-interpretation of the zonal sequence in, and along strike of, the Northern Kintyre area.

The secondary assemblages show similar mineral chemical trends to the primary assemblages. However, the later stage secondary assemblages show different trends, due to the co-existence of chlorite and K-feldspar, and the instability of biotite. In these assemblages, phengites become Al-richer with increased overprinting of these assemblages, hence Al-richer with lowering temperature, the reverse trend to what is found in the primary, and the other secondary, assemblages. Semi-quantitative phase equilibria show elegantly that
these trends are consistent.

Temperature conditions of the primary metamorphism were about 420 to 510°C in the biotite zone, and 510 to 540°C in the garnet zone. Pressure conditions were uniquely high, at 10 kbar in the biotite zone, and 10-12 kbar in the garnet zone and Northern Kintyre. These P-T conditions are further evidence of the distinctiveness of the South West Highlands region from the rest of the Dalradian. The early stages of the secondary metamorphism occurred at temperatures greater than 500°C, and at poorly constrained pressures of 6 to 10 kbar. The later stages of secondary metamorphism occurred at temperatures of about 350 °C.

Rb-Sr and K-Ar mineral age data indicate that primary metamorphism occurred at about 525 Ma ago, earlier than the primary metamorphism in the rest of the Dalradian, while the growth of albite porphyroblasts, hence the earlier stages in secondary metamorphism and deformation, occurred before 490 Ma ago, consistent with the correlation with the D₃ deformation. The age data also indicate that cooling, hence uplift, rates were slow, at about 1-2°C Ma⁻¹ in the biotite zone, and 2-4°C Ma⁻¹ in the garnet zone. Similar cooling rates are estimated from the extent of resetting of garnet zone profiles. Despite this slow cooling, high-pressure, low- to medium-temperature assemblages have been preserved.

Thermal models of the regional metamorphism in the South West Highlands show that the P-T conditions measured are attainable within the range of measured thermal properties of lithologies present in the region. Several non-unique solutions are apparent, but best-fit solutions result from the under-thrusting of a wedge of cool, low heat-producing high-grade basement gneiss beneath the Dalradian pile at the time of the primary deformation. Such a gneiss wedge is inferred from deep seismic reflection data, and its contact with the Dalradian is the West Islay Shear Belt. Hence the West Islay Gneiss, which may be part of a suspect terrane, is the surface exposure of this gneiss wedge. All the thermal models show that a pre-D₁-D₂ tectonic crustal thickening event is necessary, due to time-scales of conductive heat transfer. This thickening event is inferred by the models to have occurred at between 560 and 540 Ma ago.
This study has therefore shown that the South West Highlands had a distinct
tectono-metamorphic history, as a direct result of the distinct crustal composition
of the region. It has also shown that the early stages of Dalradian deformation
took place at depth, and that metamorphism is linked uniquely with deformation.
The earlier stages of the metamorphic history of the region were preserved, partly
because the region attained close-to-peak temperatures at this time, and partly
because post-primary deformation was restricted in extent to the deeper levels of
the crust exposed to the south-east. These levels reached higher peak
temperatures because of the lower proportion of mafic rock in the crust. The
South West Highlands is therefore a region which demonstrates uniquely the
controls on regional metamorphism.
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CHAPTER 1
INTRODUCTION AND LAYOUT OF THE THESIS

"We shall not cease from exploration...."

T.S. Eliot, Little Gidding

The study of regional metamorphism has the aim of reconstructing the thermal history and tectonic and chemical evolution of the Earth’s crust through time. Such study would normally start by characterisation of mineral assemblages and the ways in which these assemblages change petrographically, mineralogically and chemically. The definition of isograds results. Isograds are mappable lines which divide zones characterised either by the presence of an index mineral, or by specific mineral assemblages (Horne 1886, Barrow 1893, Tilley 1925, Thompson 1957). Isograds therefore define mineral reactions relating the mineralogy in the zones to either side. The pressure-temperature conditions of these reactions can be derived by use of mineral chemistry and equilibrium thermodynamics. A progressive sequence of isograds (Miyashiro 1961, 1974) will record increasing pressures (P) and temperatures (T) of metamorphism and, as a result, an apparent geothermal gradient. It must be stressed now that this gradient (or piezothermic array) never exists during regional metamorphism. It is simply the locus of P-T conditions preserved in the progressive sequence. In a metamorphic belt, the zonation is often coherent and concentric with the highest grades preserved in the core of the belt, at the lowest structural levels.

A good example of concentric metamorphic zonation is defined by Barrow’s Zones, which, with the Buchan zones (Horne 1886), represent the first attempts at mapping metamorphic rocks by the presence of index minerals. The isograd surfaces defining this zonation cut across major primary fold axes in this region, so the isograd geometry is not necessarily related to folding except on a local scale. Kennedy (1948) described the Dalradian thermal structure in terms of a thermal anticline, with the highest grade rocks buried initially at the greatest depths. A more complex thermal structure has been advocated by Chinner and co-workers (Chinner and Heseltine 1979, Chinner 1985, Watkins 1985, 1987) involving the inversion of metamorphic zones (high grade rocks above low grade rocks). Whatever the ultimate shape of this structure, its outcrop pattern (as defined by isograds) is relatively simple. This metamorphic belt is therefore well
suited as a natural laboratory for studies of the influences and controlling parameters of regional metamorphism.

Until recently, metamorphism was treated in a rather ad hoc way, in terms of fixed temperature-depth gradients and the burial and uplift of rocks. It was thought generally that the array of P-T conditions preserved in a progressive sequence recorded a real geothermal gradient in place during regional metamorphism. A good review of this point of view and its problems is given by Sutton (1963). Miyashiro (1961) recognised five Facies Series of regional metamorphism. These are arrays of peak P-T conditions defined by typical mineralogies of rocks within them, and separated and delineated in P-T space by key reactions (eg Albite = Jadeite + Quartz). Barrow’s zones are in the medium pressure Kyanite-Sillimanite facies series, while the Buchan zones are in the low to medium pressure andalusite-sillimanite facies series.

The view of regional metamorphism implicit here is that in a geosyncline, a depth-temperature gradient was in place and a rock was buried to a depth then brought back to the surface. As it was buried, its P-T conditions followed the geothermal gradient and the mineralogy adjusted accordingly. Hence reactions seen at an isograd occurred throughout the whole pile upgrade of the isograd concerned. At its maximum depth of burial, the rock recorded its maximum temperature and was then brought back to the surface (Fig. 1.1). As a result, the facies series of the sequence depended solely on the geothermal gradient. At least three major problems with this view were recognised:

1. Rocks have a measurable conductivity and heat capacity. They will not, therefore, respond instantaneously to changes in ambient temperature.
2. If a mineral assemblage reacts as the rock is buried, there would seem to be no reason why it should not undergo reaction as it is uplifted. This is a problem of kinetics. It was difficult to see why a reversible reaction should find it harder to go one way than the other. The preservation of high grade assemblages at the surface indicated the scale and nature of this problem.
3. Except in the high pressure facies series, the geothermal gradients apparently present needed high heat fluxes from the mantle to sustain them.

These questions were answered in full by England and Richardson (1977) with models of conductive heat transfer in regions of thickened continental crust. These models also introduced the absolute time dimension to regional metamorphism, together with the thermal properties of rock (eg conductivity, heat production rate, and heat capacity) and explained their role in the dynamic
Fig. 1.1 Regional metamorphism under a fixed geothermal gradient: rocks heat as they are buried, then cool as they are uplifted. In this model, the array of P-T conditions preserved in the metamorphic belt (the piezothermic array) was thought to represent the geothermal gradient. Note the "telescoping" of pressures at higher temperatures. In this model, higher grade metamorphism occurs later than lower grade metamorphism because the rocks are buried deeper and have to uplift further.

Fig. 1.2 Regional metamorphism under a geothermal gradient that varies as a result of the advection of heat by uplift and erosion: rocks follow nested P-T-t paths that intersect the piezothermic array at a high angle. The piezothermic array never exists in the crust as a geotherm, but represents the maximum entropy P-T conditions $((P-T)_{\text{max}})$. 
evolution of regional metamorphic rocks. These models could be constrained by field and laboratory-derived data (e.g., Royden and Hodges 1984), they can constrain the thermal processes operating in the crust during regional metamorphism (England and Thompson 1984) and lead to the creation of the pressure-temperature-time (P-T-t) path (Fig. 1.2). The development of P-T-t models requires geochronological data. Dempster (1984, 1985) presents a good example of such a study in the Scottish Dalradian. The studies of England and Richardson (1977) and Dempster are reviewed in sections 1.3 and 1.4 below.

This thesis presents an example of a study of regional metamorphism in which changes in P and T over relative time are extended into changes in absolute time by the use of geochronology. The study is set in the Dalradian of the South West Scottish Highlands where styles of deformation and metamorphism are relatively well constrained and where straightforward field observation reveals differences in the grade and timing of prograde metamorphism relative to the structural history in comparison with constraints that already exist for other parts of the Scottish Dalradian (e.g., Dempster 1985, Dewey and Pankhurst 1971).

A combination of geochronological, petrological, structural and petrographic information is used to construct integrated P-T-t paths and histories for contrasting parts of the area studied. The data are used to construct and constrain 1-dimensional thermal models in an attempt to explain the anomalies in the P-T conditions and history both within the study area and between it and other parts of the Dalradian.

The parameters controlling the P-T conditions and metamorphic evolution are:

1. the deep crustal structure and composition (inferred by geophysical measurements, Hall 1985; Bamford, 1979);
2. the structural level and lithological type of rocks now on the surface;
3. the variation in rates of uplift along and across strike.

Results are contrasted with what is known about other parts of the Dalradian and other metamorphic belts.
1.1 Philosophy:

The principle behind a multi-disciplinary study of this kind is simply that it provides more information and less room for ambiguity than a study using data from fewer sources. In the evolutionary view of science (Popper 1959, 1963) progress is made when contradictions to existing ideas are recognised. Experiments are carried out to reconcile and explain the contradictions resulting in a modification of the older view which renders the new information consistent with what was previously known. There is therefore a greater chance of explaining an inconsistency with a wider range of information than with a narrow range. When a scientist says that something is "correct", he or she means simply that it is internally consistent with the existing system of ideas in which he or she is working. Occasionally a system of ideas is broken down and replaced in a revolutionary manner resulting in a paradigm shift (Kuhn 1972), examples of which are the advent of Relativity in Physics and Plate Tectonics in Geology.

1.2 Time in Metamorphic Processes:

The models of England and Richardson (1977) gave rise to a paradigm shift due to the recognition of the time element in regional metamorphic processes. The original aims of the models was to explain the observation that blueschist facies series rocks are usually overprinted by medium pressure facies series assemblages and to see if sufficient heat can be generated in the crust to bring about regional metamorphism (cf. Oxburgh and Turcotte 1974) without appealling to anomalously high mantle heat flux.

The tectonic setting modelled involves the rapid thickening of crust by thrusting during continent-continent collision. This process gives rise to disequilibrium in the temperature-depth profile or geotherm resulting from balance between radiogenic heat production, heat flow from the mantle, and heat loss by conduction. It is the relaxation of this disequilibrium, accompanied by erosion-controlled uplift which results in a set of P-T-t paths followed by each of the series of rock "packets" seen on the surface.

If the piezothermic array, or metamorphic field gradient, was to represent a geothermal gradient present in the crust during regional metamorphism, it needed
enhanced heat flow rates from the mantle (Oxburgh and Turcotte 1974) to sustain it because there was insufficient crustal radiogenic heat production to balance heat loss by conduction. Implicit in this view is the idea that pressures recorded by assemblages represent the maximum pressures experienced by them, hence that maximum pressures \(P_{\text{max}}\) and maximum temperatures \(T_{\text{max}}\) are attained simultaneously. Recognition of overprinting of high pressure assemblages by medium pressure mineralogy showed that this was not usually the case. In addition, the models showed that \(P_{\text{max}}\) is only preserved with difficulty, generally if uplift rates are rapid (see also Draper and Bone 1981, and chapter 7).

Mineral assemblages record, therefore, the maximum entropy \(S_{\text{max}}\) P-T conditions, these being the P-T conditions at which kinetic conditions (strain, fluid availability, temperature, etc.) are most favourable for mineral reactions. It is accepted that \(S_{\text{max}}\) will usually be at temperatures slightly less than \(T_{\text{max}}\), and at pressures slightly less than \((P)_{T_{\text{max}}}\). Thus the \((P-T)_{S_{\text{max}}}\) conditions will generally coincide closely with the \((P-T)_{T_{\text{max}}}\) conditions. Rocks therefore follow a P-T-t path, from their \(P_{\text{max}}\) to \(T_{\text{max}}\) as erosion causes uplift and decompression during thermal relaxation and heating. As the crust reaches a temperature-depth profile close to equilibrium, continued uplift causes the crust to cool (Fig.1.2). The piezothermic array is simply the locus of \(S_{\text{max}}\) P-T conditions preserved. The nub of these models is that different "packets" of rock follow different P-T-t paths and reach \((P-T)_{S_{\text{max}}}\) at different times. The models also provide a basic mechanism for both prograde and retrograde metamorphism, giving a framework or paradigm with which to think about these processes.

Six major implications of these models are:

1. there is sufficient radiogenic heat production to sustain geotherms during medium pressure facies series regional metamorphism given sufficient time for conductive thermal re-equilibration. High mantle-derived heat flow is usually unnecessary.
2. Preservation of high pressure facies series assemblages needs high uplift rates.
3. A given metamorphic "event" will occur at different times in different parts of the metamorphic belts. Metamorphism therefore is a dynamic, evolving process.
4. If rates of uplift are similar at all times throughout an evolving metamorphic belt, low grade rocks will reach \((P-T)_{S_{\text{max}}}\) before high grade rocks.
5. The piezothermic array is concave towards the temperature axis. \((P)_{T_{\text{max}}}\) values will be telescoped at higher grades as a result.
6. \(S_{\text{max}}\) will usually occur during uplift and erosion; it occurs therefore sometime later than \(P_{\text{max}}\) and the pressures recorded in mineral
assemblages will not represent the initial depth of burial. Hence the piezothermic array has no real existence and is not represented by any geotherm present at any time during regional metamorphism. It is simply the locus of \((P-T)_{\text{S}_{\text{max}}}\) conditions preserved in the progressive sequence.

Thus, the major influences on regional metamorphic processes are rates of uplift and rates of heat production and transfer. A more rigorous view of evolving metamorphic P-T conditions therefore results from these models, the time dimension being quantifiable rather than being divided by supposedly instantaneous "events" between which relatively little is allowed to happen.

1.3 Background to the Project:

A simplifying assumption in the England and Richardson (1977) model is that uplift and heat production rates at a given level in the crust in areas undergoing regional metamorphism are constant. An implication of these assumptions is that the metamorphic grade in a given set of rocks depends on their depth of burial and that \(S_{\text{max}}\) in high grade rocks occurs later than in lower grade rocks. This is because higher grade rocks have further to go to reach \((P-T)_{S_{\text{max}}}\) and are exhumed later. In studies of the Dalradian of the Central and Eastern Scottish Highlands, Dempster (1983) showed that the opposite was the case, high grade rocks preserving older cooling ages than lower grade rocks as a result of quicker, localised uplift. This work showed the importance of detailed, integrated petrological, geochronological and structural studies of the relationships between regional metamorphism and uplift histories and tectonics, and the enhanced understanding to be gained from this sort of approach. Dempster (1984, 1985) was subsequently able to use thermal models to explain the patterns he observed. This understanding would not have been gained without geochronological information, since this resulted in recognition of early cooling in higher grade rocks.

The present study is based on the presence of along- and across-strike variation in uplift patterns and their influence on the extent, grade and timing of regional metamorphism. Fettes et al. (1986) and Graham (1986) argued that the Dalradian could be divided up into domains bounded by deep-seated lineaments whose influences can be seen in the depositional and metamorphic histories of the rocks (Fig.1.3). These contrasts are described in chapter 2; the principle aim of
Fig. 1.3 Lithostratigraphic map of the Dalradian of Scotland, with the traces of inferred lineaments. These are the loci of changes in aspects of the local sedimentological and/or metamorphic histories of the region (from Halliday et al. in press, and Fettes et al., 1986).
this thesis is to assess the roles of the contrasting deep and shallow crustal composition in controlling the orogenic history of the Dalradian metamorphic belt.

Previous work (Graham et al. 1983) shows that the South West Highlands is characterised by low to medium grade primary Barrovian assemblages but which formed under high pressure conditions (see also chapter 5). The primary assemblages formed earlier relative to the structural and deformational history of the Dalradian than the Barrovian metamorphic sequence in the Central Highlands (see also chapter 3). The contrasts in the conditions and the timing of primary regional metamorphism are correlated very strongly with the composition of the deep and shallow crust, these contrasts being separated by the Cruachan Lineament.

1.4 Layout of the Thesis:

Chapter 2 reviews the general geology and geography of the study area including comparisons and contrasts between the structural histories of the South West and the Central Highlands. Chapter 3 discusses the primary metamorphism concentrating on reactions, assemblages, isograds, phase equilibria, and the relationships between metamorphism and the structural history. Secondary, overprinting metamorphic assemblages are discussed in chapter 4. The textures and timing of growth in relation to the regional structural history is discussed first, followed by a description of the chemistry, mineralogy and reactions of these assemblages. In chapters 3 and 4, qualitative changes in P-T conditions are discussed. Quantitative P-T estimates are made in chapter 5 where a variety of geothermobarometers are applied.

Chapter 6 deals with the geochronological component of this study. Firstly, there is a critical review of the closure temperature concept and the techniques and assumptions behind the methods used in this and other studies. Then, the geochronological data are presented in the light of the conclusions drawn from the review of closure temperatures and methods. These data are then compared with data from other parts of the Scottish Dalradian, especially from Dempster (1984, 1985) putting absolute time values on to the P-T-relative time history derived in earlier chapters. Chapter 7 reviews thermal models for metamorphic
belts from England and Richardson (1977) onwards, then presents the results of 1-dimensional heat conduction modelling, as applied to the South West Highlands. These models are based on England and Richardson (1977). Chapter 8 synthesises the results from the previous chapters and draws the necessary conclusions for the P-T-t evolution of the area. Comparisons are drawn also with the Central Highlands and other metamorphic belts. The thesis is concerned therefore with the construction of detailed P-T-t paths using data from a variety of sources, each chapter describing and discussing a stage in this P-T-t history.
CHAPTER 2
THE DEPOSITIONAL AND DEFORMATIONAL HISTORY OF THE DALRADIAN

"It's only half completed, I'm afraid, we haven't even finished burying the artificial dinosaur skeletons in the crust yet, then we have the Tertiary and Quarternary periods of the Cainozoic Era to lay down......."


This chapter is devoted to the establishment of the geological framework on which the study of the metamorphic and thermal history of the South West Highlands is based. It will highlight the contrasts in the stratigraphic and structural histories found both within the area, and between the area and other parts of the Dalradian. It starts with an outline of the stratigraphy of the Dalradian, this being the history of the sedimentological evolution. Links between lithologies outcropping on the present-day surface and the composition of the middle and lower crust will be drawn and described. Because of the probable strong links between these two factors and the subsequent structural and metamorphic histories, the contrasts seen in lithology and crustal composition seen within the area will be highlighted.

There will then follow a description of the structural evolution of the area which also shows contrasts in complexity both within and between the area studied, and other parts of the Dalradian and is again linked with the factors controlling metamorphism. This chapter is based largely on other detailed studies of the sedimentology and tectonics.

2.1 Geography of the Study Area:

The study area is located in the South West Highlands of Scotland, in what was known as the County of Argyll (Fig. 2.1). It is concentrated mainly in the Tayvallich, Knapdale, and Northern Kintyre areas, although samples were also collected from Jura, Islay, and the Cowal (Dunoon-Holy Loch) areas, all of which
Fig. 2.1 Location map of the study area with key locations and places mentioned throughout this thesis.
are now part of Strathclyde Region. In contrast with the rest of the Highlands, most of the country is below 500 metres in elevation, the most mountainous areas being South West Jura (at 800 metres) and South East Islay. Exposure is good to excellent along all coasts and weathering of rocks is not a major problem. Inland, exposure is good on higher ground to non-existent on the lowest areas (between Crinan and Lochgilphead, Knapdale, and the Loch Gruinart area, Islay). In the higher inland areas, most of the ground is moorland and weathering is more troublesome than on the coast. Some parts are forested making access difficult, although no part of the area is more than five miles from a metalled road.

The West coast of Knapdale is cut by two long sea lochs; Loch Sween and West Loch Tarbert. In addition, the Tayvallich Peninsula is cut by several inlets and separated by these from the country to the South. The whole area is separated by Loch Fyne and Loch Gilp from the country to the East. As a result, there is a long coastline with good exposure and good access. The basic geological relations are well constrained as a result of the British Geological Survey mapping as well as more recent detailed study of specific areas (Wilson and Leake 1972, Roberts 1974, Anderton 1979, Fitches and Maltman 1984)

2.2 Stratigraphy:

The Dalradian Supergroup (Harris and Pitcher 1975) is a lithologically diverse sequence estimated to have a cumulative stratigraphic thickness of up to 25 km. Dalradian rocks are exposed in Western and Northern Ireland as well as in the Southern and Eastern Highlands of Scotland. According to the correlation of Harris and Pitcher (1975, 1978), the Dalradian can be divided into four groups. These are; the Grampian, Appin, Argyll, and Southern Highland Groups in younging order. Piasecki and van Breeman (1983) divided the Grampian Group into two, the Central Highland Division and Grampian Division in younging order. This division was based on the recognition of Morarian (van Breeman et al. 1978) tectono-thermal activity in the underlying Central Highland Division, activity which is absent in the Grampian Division. These two divisions are separated by the Grampian Slide. The Grampian Division is also sedimentologically continuous with the Appin Group, so this correlation scheme is adopted for this thesis.

Figs 2.2 and 2.3 summarise the stratigraphic framework and need to be
Fig. 2.2 Simplified lithostratigraphic map of the Scottish Dalradian Supergroup (from Harris et al. 1976):
Fig. 2.3 Stratigraphical column for the Dalradian of the South West Highlands (from Harris et al. 1976):

Fig. 2.4 Simplified cross-section of the chronostratigraphic horizon represented by the Easdale Slate and the Scarba Conglomerate. The thickness and sedimentological variations are caused by syn-depositional growth faulting (from Anderson 1979).
inspected together. The rocks studied in this thesis range in stratigraphic age from
the Ballachullish subgroup, in the Appin Group, to the middle of the (undivided)
Southern Highland group. The Dalradian groups are subdivided into subgroups
which in turn are subdivided into formations named after the specific rock type
that is dominant and the locality at which the formation is best developed. The
formations marking the bases of the Dalradian groups are the Eilde Quartzite, the
Port Askaig Tillite and the Tayvallich Volcanics. The names of the Dalradian
formations are lithostratigraphic and do not have strict chronostratigraphic
significance. As a result, due to the often great lateral variation in sedimentology
in a number of formations (eg Anderton 1979), lithostratigraphic names vary for a
given position in the stratigraphic column. For example, the Tayvallich volcanics
and the Loch Avich Lavas pass laterally into the volcaniclastic sedimentary
horizons, the Green Beds, and the Loch Tay Limestone is laterally equivalent to
the Tayvallich Limestone.

Harris et al. (1978) showed that Grampian Division and Appin Group
sediments were deposited on a stable shelf within a trough variably restricted with
respect to sedimentary infill. Grampian Division flaggy sandstones were deposited
first, followed by Appin Group silts, muds, clays, carbonates and black shales.

The base of the Argyll Group is marked by a thin but laterally continuous
boulder bed which is generally accepted as being a tillite horizon, the Port Askaig
Tillite, resulting from dropstones from ice sheets during a late pre-Cambrian
glaciation period. This Tillite was followed by the Bonahaven Dolomite, and the
coarse clastic but texturally mature (low modal feldspar and well sorted) Jura
Quartzite. The latter sometimes shows crossed and graded bedding and variation
in grain size between beds. Thus the environment so far has been one involving a
shallow to deep shelf which has so far been relatively stable, although variations in
depth and clastic input have occurred (Harris et al. 1978).

Tectonic instability then set in with the two laterally equivalent but very
different horizons, the Scarba Conglomerate and the Easdale Slate. The
sedimentology of these Formations was described in detail by Anderton (1979).
They were depth-controlled by syn-depositional faults across which major facies
changes took place. These faults were inferred by thickness variation as shown on
Fig. 2.4 (Anderton's Fig. 1). The faults had trends both parallel (north-east to
south-west) and perpendicular (north-west to south-east) to the regional strike, as
shown on the figure and marked the onset of major subsidence.
The tectonic instability of the depositional environment continued with the depositon of coarse, clastic immature sediments; the Crinan Grit which pass laterally into the Erins Quartzite. While sedimentary structures are well developed in the Crinan Grit, with cross and graded bedding, the Erins Quartzite is sufficiently deformed and metamorphosed to make recognition of such structures difficult. However, the two horizons are distinct sedimentologically, the Crinan Grit having coarse conglomeratic and pebbly bands as well as a greater modal abundance of clastic feldspar. Thus the Crinan Grit was probably a proximal equivalent to the Erins Quartzite. Mafic sills and dykes were emplaced in these horizons making up a large proportion of the thickness of the succession. Structural reconstruction studies on the dykes (Graham and Borradaile 1984) show that they had a trans-caledonoid (north-west to south-east) trend during emplacement implying, with the faulting recognised by Anderton (1979), a transtensional component to the rift-associated stretching of the Dalradian basin.

The Argyll Group to Southern Highland Group transition occurred with the emplacement of the Tayvallich Volcanics which are associated with the deposition of shales and limestones. The shallow, high energy nature of the depositional environment is evident from the presence of subaerial hyaloclastites (Gower 1977) and breccias with clasts of 10-100 cm size. The Tayvallich Volcanics were locally developed, their lateral equivalents being volcanigenic clastic sediments, the Green Beds. The volcanic horizon was therefore concentrated to the north-west. The trace element (Graham 1976, Graham and Bradbury 1981) and isotopic (Halliday et al. in press) characteristics of these lavas shows they are tholeitic and are similar geochemically to modern lavas associated with incipient rifting. The correlation between the presence of extrusive rocks and low clastic input is also clear and leads to comparison with the present-day Baja California (Einsele 1985, Graham 1986) where very high sedimentation rates prevent magmas from reaching the surface before their crystallisation. Both sills and lavas are sometimes spilitised resulting in high Na abundances and nepheline in the normative composition (Fig. 2.5: Graham 1976).

Rifting-associated magmatic activity paused during the deposition of turbiditic deposits, the Beinn Bheula Schists/Loch Avich Grits. In the north-west, this subgroup is overlain by the Loch Avich Lavas. Graham and Bradbury (1981) suggested a south-easterly source for the clastic input of the Loch Avich Grits based on the presence of high grade metamorphic clasts similar to xenoliths found
Fig. 2.5 Na abundances v. modal and normative feldspar in syn-depositional mafic rocks from the South West Highlands: the spilitised rocks have high Na abundances (from Graham 1976).

Fig. 2.7 Cartoon of trans-tensional basin development model whereby stretching and crustal instability are concentrated along the Cruachan Lineament and precursor lineaments to the Highland Border Fault (from Graham 1986).
In summary, Dalradian sedimentological evolution occurred in an environment whose depocentre underwent major variations in depth both laterally and with time, as well as becoming increasingly unstable tectonically, culminating in the emplacement of rift-related volcanics (Fig. 2.6). All these features point to an evolving basin environment with increasing crustal stretching leading to incipient rifting. According to the models of Dewey (1982), based on McKenzie (1978) and Royden (1982), the presence of syn-rift lavas implies a $B$ value (degree of stretching) substantially greater than 2. Tectonically, the depositional environment was transtensional, stretching occurring dominantly in a north-west to south-east direction but with a significant strike-slip component. Graham (1986) in arguing for the presence of a syn-depositional break in the crust, suggested that rifting took place along this break, and lineaments sub-parallel to the Highland Border Fault (Fig. 2.7).

The major implication of the tectonic instability accompanying Dalradian deposition is the great lateral and vertical facies variation exemplified by the study of Anderton (1979) as well as the localised emplacement of the Tayvallich Volcanics. This thesis will show that the influences of the lithological contrasts formed during Dalradian deposition were all-pervasive during deformation, metamorphism and orogeny.

2.3 Contrasts in the Depositional Histories; Lineaments:

Although most horizons within the Dalradian can be correlated for long distances along strike (eg the Loch Tay Limestone), many horizons are laterally discontinuous, a good example of lateral sedimentological discontinuity being that described by Anderton (1979). In addition, thicknesses within a lithostratigraphic subgroup or member will vary (eg Borradaile 1979). Thus, much of the sedimentology of the Dalradian was controlled by faults. While some of these faults are syn-depositional (as inferred by facies and thickness variations), and affect local areas only, others are more deep seated and affect the subsequent structural and metamorphic histories, as well as being influential during the deposition. These deep seated discontinuities, or lineaments, are recognised generally by breaks in one or more of the geochemical, structural, metamorphic
Fig. 2.6 Summary of the tectonic history of the Dalradian, with times of emplacement and deposition of igneous horizons (from Harris et al. 1978):
and sedimentological patterns developed in the sequence. The existence of several lineaments in the Dalradian was postulated by Fettes et al. (1986).

The two largest lineaments of those inferred by Fettes et al. are the Cruachan Lineament (Hall 1985, 1986, Graham 1986), and the Portsoy-Duchray Hill Line (Ashcroft et al. 1984, Harte 1988 in press) (Fig. 2.8) Both of these lines are apparent from geophysical and geochemical data (Figs 2.9 and 2.10) and they separate zones of contrasting depositional, structural and metamorphic histories. The Cruachan Lineament separates the South West Highlands from the Central and Southern Highlands and its presence has apparently affected the depositional environments and facies in ways to be described below. The resultant variations in lithology and crustal composition have influenced the metamorphic and structural histories developed in the Dalradian, as will be re-iterated and developed throughout this thesis. The existence of the Cruachan Lineament is the key, therefore, to the contrasts and variations dividing the South West Highlands Dalradian from the rest of the Scottish Caledonides and it will be discussed in detail in this section.

2.3.1 Contrasts in Facies Development and Depositional History:

Fettes et al. (1986) point out that most of the local-scale facies changes and variability in the Dalradian occurs within the Argyll Group. The Appin Group was deposited in a stable environment and the sedimentary facies of the Southern Highland Group are relatively uniform, although instability is indicated by the turbiditic natures of these rocks. The lithological variability in the Argyll Group obviously makes recognition of facies changes and tectonic breaks easier to recognise, but large scale lateral variation is present in the Southern Highland Group. This variation is recogniseable over longer distances along, and across, strike than in the Argyll Group and is most apparent in the horizons equivalent to the Tayvallich Volcanics and the Loch Avich Lavas. The extrusive components of these horizons are locally developed towards the north-west of the South West Highlands area and their distal equivalents to the south-east are the Green Beds.

Across the Cruachan Lineament, the proportion of the stratigraphic thickness made up of syn-depositional mafic igneous rock is reduced from 20 to 30% in the South West Highlands to substantially less than 5% in the Central Highlands (Graham and Bradbury 1981). In the South West Highlands, the mafic volcanics
Fig. 2.8 Lithostratigraphic map of the Dalradian with the traces of the Cruachan and Portsoy-Duchray Hill Lineaments (from Halliday et al. in press, and after Fettes et al. 1986).
are concentrated in the core of a major primary fold, the Loch Awe Syncline (below, section 2.5), while accompanying syn-depositional sills in horizons below the volcanics stratigraphically are also predominant in this area.

Fettes et al. (1986) also describe contrasts across the Cruachan Line in the sizes of the basins in which the Dalradian sedimentation occurred. Those basins to the south-west of the Cruachan Line are developed on larger than 10 km scales, while to the north-east, they are substantially smaller. This implies, according to Fettes et al., that greater extension of the crust occurred in the south-west, with a higher degree of thinning affecting a greater volume of the crust. This, of course, is consistent with the emplacement of mafic igneous rocks in the south-west, including volcanics. Thus, while syn-depositional rifting and faulting are not apparent in the sediments of the Southern Highland Group, its presence at this time is indicated by these mafic rocks, the Tayvallich Volcanics and the Loch Avich Lavas, whose exposure appears to be cut by the Cruachan Line.

Treagus and King (1978) have shown that a fully-developed but thinned Dalradian stratigraphic sequence is developed in the Central Highlands where the base of the Appin Group is emplaced over the Grampian Group metasediments. The attenuation was caused by sliding (Treagus 1987), but the presence of a recognisable sequence of Dalradian stratigraphy from Appin to Southern Highland Groups but without the large volumes of mafic rock in the south-west indicates that mafic rocks never made up a large proportion of the Dalradian Supergroup in the Central Highlands, to the north-east of the Cruachan Line.

Graham (1986) suggested that the initial stages of the rifting in the South West Highlands had a strong trans-tensional component, with the Cruachan Lineament being the locus of rifting. This argument was based on Anderton (1979) - who found evidence for trans-Caledonoid syn-depositional faulting - and on Graham and Borradaile (1984) who recognised trans-Caledonoid trends in feeder dykes to the mafic volcanics and sills. However, the present-day exposure of volcanic horizons has a strong north-east to south-west trend. This trend is not due entirely to the folding history and alignment of fold axes, due to the absence of similar rocks in the equivalent horizons to the south-east. As a result, Graham argued that rifting would have been a strike-slip regime in its earlier stages, but would have developed an across-strike component of rifting in its later stages. The Cruachan Lineament separates crustal domains with contrasting sedimentological histories, and with contrasting composition as a result.
2.3.2 Contrasts in the Deep Crustal Structure; Geophysical Evidence:

While the composition of the Dalradian, hence that of the upper part of the continental crust in the region changes across the Cruachan Lineament in the manner just described, a variety of lines of geophysical evidence suggests that these changes are more profound in every sense, being reflected in the structure and inferred composition of the lower continental crust. The geophysical evidence comprises magnetic, gravity and seismic data taken over both local and regional scales. Each of these lines of evidence will be described in turn.

Westbrooke and Borradaile (1978) studied the structure and composition of the crust in Islay, with particular reference to the contact between basement "Lewisianoid" gneiss and the overlying Caledonian metamorphic rocks. While on the surface, it is apparent that Dalradian rocks are emplaced over the basement gneiss with only a small thickness of intervening rock, the Bowmore Sandstone, between them, Westbrook and Borradaile showed that this relationship was continuous at depth (Fig. 2.11).

Fitches and Maltman (1984) have shown that the Loch Skerrols Thrust, inferred by Westbrooke and Borradaile as being the contact between the Dalradian and the basement rocks, is actually a local-scale slide forming a part of a belt of high shear strain affecting much of Islay. It can be argued, however, that the data of Westbrooke and Borradaile (1978) cannot rule out the possibility that an equivalent to the Moine Thrust Belt is present at depth along with Moine rocks, because the Loch Skerrols "thrust" is not equivalent to the Moine Thrust Zone (Fitches and Maltman 1984, this thesis section 2.5). Information is needed, therefore, which improves the constraints on the deep crustal structure. This is provided by regional-scale gravity data (Hipkin and Hussein 1982) and deep seismic reflection and refraction data (Bamford 1979, Hall 1985).

The structure of the regional gravity field in the Caledonides shows a number of anomalies and variations, one of the largest of which is the rapid change from a positive Bouger gravity in the south-west to a negative Bouger gravity in the north-east, across the trace of the Cruachan Lineament (Fig. 2.9). While in the Central Highlands, there are many granite plutons intruded during and after the deformation and metamorphism of the Dalradian (eg Pidgeon and Aftalion 1978), no such plutons are present in the South West Highlands, except for the small
Fig. 2.9 Bouger gravity anomaly map of Scotland: note the steep change in gravity across the trace of the Cruachan Lineament (from Hall 1985).

Fig. 2.11 Schematic crustal structure of the South West Highlands derived by aeromagnetic mapping: the Dalradian is emplaced directly onto a high grade gneissic basement exposed in Western Islay (from Westbrooke and Borradile 1978).
Fig. 2.10 Regional geochemical maps of the Scottish Highlands: note the changes across the Dalradian (Dal.) - Central Highland Division (C.H.D.) contact, and across the Cruachan Lineament (C.L.).
Kilmelford intrusion (eg Halliday et al. 1984). The only igneous rocks present to any scale in the south-west are the Tayvallich and Loch Avich Suites. Since basic igneous rock tends to be more dense than acidic, much of the gravity variation can be explained in this way. However, the gravity field contrasts are also present towards the Highland Border, where few igneous rocks are present; larger scale contrasts in the crustal composition therefore need to be invoked to explain these observations.

Hall (1986) presented two probable, but contrasting interpretations for the gravity field changes (Fig. 2.12). Fig 2.12(a) suggests that the Dalradian is of constant thickness throughout the Scottish Highlands, but that the proportion of the crust made up by Caledonian metamorphic rocks in the Central Highlands is increased by Moine metasediments at depth overlying directly the basement gneisses. Fig. 2.12(b) suggests, however, that the Caledonian metamorphic component of the crust is of similar thickness in both the Central Highlands and the South West Highlands. Thus, the two alternatives are either that the Dalradian is thinner in the Central Highlands, or that basement gneisses make up a greater proportion of the total crustal thickness in the South West Highlands. Both alternatives imply that the Moine (Central Highland Division) and, perhaps, the Grampian Division are absent in the South West Highlands.

The section through the crust for which this model was constructed runs parallel to, but about 20 km to the north-west of, the Highland Boundary Fault. It therefore does not include the Cruachan Granite or the Dalradian lavas and sills. The density contrasts in this model are due mainly to large scale variations in the crustal structure. However, the contrasts in density further towards the north-west will be enhanced, by the increasing densities of the crust in the South West Highlands, as the Tayvallich and Loch Avich Suites are reached. This information therefore implies that the Central Highland Division and probably the Grampian Division are absent at depth and that the crust is denser in the South West Highlands being at its most dense near to Tayvallich and Loch Awe. However, it is not clear, on the evidence presented so far, how thick the Caledonian metamorphic rocks are in the South West Highlands, nor in the Central Highlands.

Further information on the deep crustal structure has been derived by seismic reflection and refraction profiling. Banford (1979) described a north-to-south directed profile across the Central Highlands, as part of the LiSPB deep seismic
Fig. 2.12 Two possible models for the contrasting deep crustal structure in the South West and Central Highlands (from Hall 1985):

(a) constant thickness Dalradian throughout, but with "Moine" (Central Highland and Grampian Division) crust between the Dalradian and the crustal Basement in the Central Highlands:

(b) Caledonian (Dalradian and "Moine") rocks are the same thickness in the South West Highlands and the Central Highlands, but are underlain by thicker basement in the South West.

Fig. 2.13 Simplified interpretation of the WINCH profile: major reflectors represent thrust planes caused by flake tectonics; a wedge of basement gneiss, now exposed in Western Islay, is thrust between the Dalradian and the base of the crust (from Hall 1985). Note that the crust is thinnest along-strike of the Tayvallich region: this profile favours the interpretation in Fig. 2.12(a) (from Hall 1985).
refraction profile across Britain, while Hall (1985) described the WINCH reflection profile to the west of Islay. Both of these profiles therefore intersect the regional strike at a high angle. At the present-day, the Moho is at a depth of 25 to 30 Km in the WINCH profile and the crust is at its thinnest directly beneath the exposure of the Tayvallich Volcanics. Here, the lowest layer in the crust is attenuated and thinned to a thickness of 8 to 10 Km. The middle layer in the crust is similar to basement gneiss and thickens to the north-west and to the south-east as a result of "thin skinned" or "flake" tectonics. The upper layer in the crust is made up of Caledonian metamorphic rocks and is up to 10 Km thick in the south-east. The upper crustal layer is emplaced onto the middle layer along a south-east dipping shallow contact, which is exposed on the surface as the Loch West Islay Shear Belt (section 2.5).

Thus, compression occurring at some stage in the Caledonian orogeny was taken up by these very large scale tectonic features, as well as the folding which occurred within the Dalradian and Moine crust now on the surface. The crust is thinnest at Tayvallich and Loch Awe, where the most mafic and densest crust is present. To the south-east, the crust is more intermediate and thicker. The interpretation of the WINCH profile is shown in Fig. 2.13.

The crust in the LISPB profile ranges from 30 to 35 Km thick and is made up of a similar three-layered structure (Fig. 2.14), the contrast being that the upper layer of Caledonian metamorphic rocks is thicker than in the South West Highlands and does not vary in thickness. The lowest layer thins significantly towards the Great Glen Fault Zone. Contrasting "layer cake" models of the crust in the Central and the South West Highlands are shown in Fig. 2.15. The WINCH profile shows no evidence of thrust slices of Moine rocks at depth, the upper crustal layer rests directly on the middle basement gneiss layer, which in turn rests on the lower mafic crustal layer.

Taken together, the geophysical evidence for the nature of the crust in the Scottish Highlands shows that the crust in the South West Highlands is about 5 Km thinner than in the Central Highlands. It is also denser, and the proportion of metasedimentary rock in the upper layer (Caledonian metamorphics) is less. Since the Central Highland Division, and probably the Grampian Division are apparently absent to the south-west of the Cruachan Lineament, but present on the surface and at depth in the Central Highlands, the gravity model in Fig. 2.12(a) is a close approximation to the gross crustal structure in the region. The
**Fig. 2.14** Interpretation of the LISPB profile: the crust has a three-layered structure with Caledonian metamorphic rocks lying on a gneissic layer, lying in turn on the base of the crust (from Bamford 1979).

**Fig. 2.16** U-Pb concordia diagram for zircon analyses from Tavullich: the upper intercept is near 595 Ma, while the lower intercept is at zero (from Halliday et al., in press).
Fig. 2.15 contrasting “layer cake” sections through the crust in the Central Highlands and the South West Highlands.
crust in the Scottish Highlands therefore displays heterogeneities on most scales from a few km (high abundances of mafic rock in and around the Loch Awe region) to a few hundred km (high abundances of semi-pelitic and psammitic metasediments in the Central Highlands, less to the south-west) and is also heterogeneous on depth-scales from near-surface to the entire crust. In the Dalradian, the crust is heterogeneous on small to large scales and in three dimensions, and the variation arose as a result of the contrasts in the depositional history.

2.4 Time Constraints on Dalradian Deposition:

Because the Dalradian is a dominantly coarse clastic sequence, preservation of faunal evidence on the time of deposition is poor. There are three major carbonate horizons, the Islay Limestone, the Bonahaven Dolomite, and the Tayvallich Limestone, which are unquestionably Dalradian. The Leny Limestone, from which the well-known trilobite fauna have been found, is considered by B.J. Bluck (1988, pers. comm.) to be fault-bounded by Dalradian and Highland Border Complex rocks. The Dalradian bedding, according to Bluck strikes directly into the contact with the Leny Limestone, and shearing is present in rocks found between the Dalradian and Leny Limestone exposures. Sparse acritarch fauna have been recognised in the Bonahaven Dolomite and the Tayvallich Limestone (Downie et al. 1971), to which Vendean (late Precambrian) to lower Cambrian ages have been assigned. Upper Riphean to Vendean stromatolites have been yielded to Spencer and Spencer (1972) from the Islay Limestone.

Absolute timing by radiometric ages has also been sparse and equivocal. The Port Askaig Tillite is generally correlated with the Varanger Tillite, Northern Scandinavia which has been dated at 668 ±23 Ma by Pringle (1972) using the Rb-Sr whole rock isochron method. Although this is not entirely inconsistent with the fossil evidence in the Islay Limestone and Bonahaven Dolomite, the uncertainty over both the geochronological data (due to possible resetting by metamorphism) and faunal interpretation (due to the long-ranging distribution of the species found) is still very great.

At Tayvallich, keratophyre plugs described by Gower (1977) are associated with the volcanic and carbonate horizons as are coarse breccias with similar
keratophyre clasts showing that these plugs are syn-depositional. Trace element analyses of these plugs by Graham (1974) and Wilson and Leake (1972) showed that they had very high zirconium values as a result of the extreme fractionation of the Tayvallic suite described by Graham (1976). They were therefore likely to have had high modal zircon, and, as a result, be suitable for U-Pb dating.

Samples from one keratophyre plug from Tayvallich Peninsula were collected by Dr. C.M Graham, Dr. A.N. Halliday and myself and zircons were separated from these and analysed for U-Pb dating by Dr. M. Aftalion (see Halliday et al. 1988 in press for methods). Four size fractions of euhedral, magmatic zircons were analysed giving a series of discordant ages with an upper intercept of 596 ± 5 Ma whether by fixing the lower concordia intercept at zero Ma or by least squares fit (Fig.2.16). This age represents by far the best chronostratigraphic constraint available on Dalradian sedimentation, especially as the Tayvallich Volcanics and their lateral equivalents are taken as marking the base of the Southern Highland Group.

Due to the sparseness of faunal evidence, it is difficult to relate this datum to the broader Precambrian-Cambrian timescale, except to say that if the base of the Cambrian is at 570 Ma, the whole of the Argyll Group is Precambrian in age (cf. Downie 1975) and the datum implies that Dalradian deposition tends to be earlier than generally thought. The fossil evidence of Spencer and Spencer (1972) (upper Riphean to Vendean stromatolites in the Islay Limestone) is most consistent with this datum. Further details are found in Halliday et al. (in press: pre-print at back of thesis). One of the more important results of these data is that the timing of Dalradian deposition is fixed with accuracy in absolute time, meaning that this can be related to the constraints on burial, deformation and metamorphism to be presented in the rest of this thesis.

The onset of Dalradian deposition is also poorly constrained. No evidence of Morarian tectono-thermal activity is found and Piasecki and van Breeman (1979) used the absence of this event to subdivide the Grampian Group of Harris et al. (1978) into the Central Highland Division and Grampian Division, separated by the Grampian Slide. The Morarian event, developed in Central Highland Division rocks, is set by a number of published (Piasecki and van Breeman 1979, 1983) and unpublished (E. Hyslop, M.A.J. Piasecki, pers. comms.) geochronological data on shear zone pegmatites at about 750 Ma. Soper and Anderton (1984) suggested that these shear zones may mark the onset of rifting associated with formation of
the Dalradian basin. All the information in this section suggests that Dalradian deposition started at 750 Ma at the earliest and was still continuing at 595 Ma, lasting at least 155 Ma. Obviously, no constraint on when Dalradian Deposition ceased is available, but given the turbiditic nature of much of the Southern Highland Group sediments, these may have been laid down relatively quickly. In that time, a sequence with a cumulative thickness of up to 25 km was laid down. The chronostratigraphy of the Dalradian based on the new U-Pb zircon data and the paleontological information described is presented in Fig. 2.17.

2.5 Deformation in the South West Highlands:

In this section, the structures in the area will be described, based largely on the studies of Roberts (1974) in the Tayvallich, Knapdale and Northern Kintyre areas, and Fitches and Maltman (1984) on Islay and Colonsay. The deformation patterns in the South West Highlands will be compared with those in the Central Highlands, then the structural history of the South West will be summarised with a view to elucidating the mechanisms and controlling factors of the nucleation, growth and propagation of the major folds seen in the area. The structural history as told in this chapter will be used in subsequent parts of the thesis as a framework for the regional metamorphic history to be presented.

2.5.1 Historical Perspective:

The scale and complexity of the Dalradian depositional history has been illustrated in the previous section. Because Dalradian sedimentation shows great diversity laterally as well as vertically, correlation of horizons developed at disparate parts of the sequence has proven to be difficult, and recognition of major folds has relied to a great extent upon the scheme of correlation adopted. However, a consensus has emerged, over the large scale form of Dalradian structures. A steep zone of bedding and fabrics is recognised separating two shallower zones of folds and slides verging north-west and south-east-wards from the steep zone (Fig. 2.18). There is still much controversy over the form and role of the steep zone, particularly over where the steep zone in the South West Highlands (the Knapdale Steep Belt, Roberts 1974) runs to the north-east, into the Central Highlands. Thomas (1979) and Anderton (1988) both suggested that the
Fig. 2.17: Time constraints on the depositional history of the Dalradian, based on the faunal and geochronological evidence discussed in the text:

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>Constraint</th>
<th>Lithostratigraphic Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>≈ 570 Ma</td>
<td>(Trilobite Fauna)</td>
<td>(Leny Limestone)</td>
</tr>
<tr>
<td>596±5 Ma</td>
<td>U-Pb zircon age data</td>
<td>Tayvallich Volcanics</td>
</tr>
<tr>
<td></td>
<td>Acritarch Fauna</td>
<td>Tayvallich Limestone</td>
</tr>
<tr>
<td></td>
<td>Acritarchs</td>
<td>Bonahavan Dolomite</td>
</tr>
<tr>
<td>668±23 Ma</td>
<td>Rb-Sr whole-rock isochron</td>
<td>(Port Askaig Tillite)</td>
</tr>
<tr>
<td></td>
<td>Stromatolites</td>
<td>Islay Limestone</td>
</tr>
<tr>
<td>&lt; 750 Ma</td>
<td>Morarian Ages</td>
<td></td>
</tr>
<tr>
<td>&gt; 750 Ma</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.18  Contrasting gross structural styles and development along-strike in the Dalradian. North-west and south-east verging structures are separated by a Zone of Divergence which forms a moderately open, upward-facing fold in the South West Highlands, and upright to reclined, very tight, north-west- to upward-facing folds elsewhere. Localities: (a) Schiehallion (Treagus 1987); (b) Ben Alder (Thomas 1979); (c) South West Highlands (Roberts 1974):
steep zone is continuous at least as far north-east as Ben Alder, manifest there as the Ossian Steep Belt while Roberts and Treagus (1979) and Treagus (1987) argue that the steep zone in the South West Highlands cannot be traced beyond Ben Cruachan.

Bailey (1922) was the first study to attempt a regional synthesis of Dalradian structures, as well as the first to invoke the Nappe concept. This concept suggests that crust having undergone orogeny is made of sequences of rock, which may be flat lying or folded, separated by tectonic contacts or slides. The presence of slides was invoked by Bailey as an explanation for lithological and stratigraphic breaks and discontinuities implying that the rocks as seen now are essentially allochthonous with respect to one another. Bailey divided the Dalradian into the Loch Awe Nappe, the Iltay Nappe and the basal Ballapel formation, from the structural top to the structural base of the sequence. The Loch Awe Slide separated the Loch Awe Nappe from the rest of the sequence, while the Iltay Boundary Slide separated the the Iltay Nappe from the Ballapel Formation.

On a broad scale, the only difference between Bailey’s view and the current view is the status of the Loch Awe Nappe and Slide, it now being believed that the Loch Awe Slide does not exist, and that much of the sequence now exposed has been inverted (Shackleton 1958). The general concept of nappes separated by slides is still in force, with the Tay Nappe corresponding to a large extent to the Bailey's Loch Awe and Iltay Nappes, and the Iltay Boundary Slide forming a base to the Appin Group in the Central Highlands, now called the Boundary Slide.

The other major difference between Bailey’s view and the current view (eg Roberts 1974, Thomas 1979, Roberts and Treagus 1979, Treagus 1987) is that Bailey regarded a number of major folds, now believed to be primary, as secondary modifications of the Nappes he was invoking. Two nappes are now recognised in the South West Highlands, the Tay Nappe, facing to the south-east, and the Islay Anticline, facing to the north-west. While the base of the Tay Nappe is not exposed, the Boundary Slide, the Fort William Slide and the Loch Skerrols Shear Zone (formerly recognised as a thrust; below, 2.5.2) are seen as bases to the Dalradian Nappes north-west of the respective steep zones in each area. (Treagus 1987, Fitches and Maltman 1984). The point should be made that these slides emplace younger rock onto older rock and therefore cannot be thought of as thrusts in the strict sense (Soper and Anderton 1984) since, by definition, thrusts reverse stratigraphy.

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There now follows a description of the structures developed in the South West Highlands as seen in Islay and Colonsay, Tayvallich, Knapdale and Northern Kintyre. Comparisons between these areas and the Central Highlands will be made in section 2.6.

2.5.2 The Primary Deformation:

The deformational history of the Scottish Dalradian is generally divided between a primary, nappe forming event and a secondary phase involving modification of the large scale geometry of the primary folds (eg Roberts 1974). Three large scale folds of bedding were formed and emplaced during the primary deformation. These are, in order from the North West to South East, the tight to isoclinal north-west-facing Islay Anticline, the moderately open upward facing Loch Awe Syncline and the inclined to recumbent isoclinal Ardrishaig Anticline (whose fold closure is seen as the downward-facing Aberfoyle Anticline and associated folds; Shackleton 1958, Harte et al. 1984, Mendum and Fettes 1985).

These three folds control the outcrop pattern, resulting in large scale inversions of bedding in the lower limbs of both major nappes in the region (Islay Anticline and Ardrishaig Anticline).

Traces of the fold axes of these folds are shown on Fig. 2.19, together with a cross-section of their geometry. This cross-section shows clearly the mushroom-shaped geometry of the folds; the Tay Nappe rooting in the Ardshaig Anticline and the Loch Awe Syncline defining the steep zone in the South West Highlands (cf. Thomas 1979, Bradbury et al. 1979). To the north-west, the Islay Anticline roots in a similar manner to the Loch Awe Syncline but has a more upright attitude. As will be discussed in 2.3.5 below, all of these folds have had their geometry modified by the secondary phase of deformation.

Associated with the primary folding is a strong, regionally developed axial planar cleavage. This has a variable attitude, fanning across the Loch Awe Syncline from a horizontal attitude in Western Islay, through the vertical in the Loch Awe syncline to a steep north-west dip in the Ardrishaig Anticline. The cleavage is folded by the secondary compound Cowal Antiform (2.3.5 below).
Fig. 2.19 Traces of the major primary fold axes in the South West Highlands: The Islay Anticline and Ardrishaig Anticlines represent the traces of the north-west, and south-east verging major structures in the region respectively, while the Loch Awe Syncline is the steep zone (from Roberts 1974).

Fig. 2.20 Structural block diagram of Jura, Islay and Colonsay with the Islay Anticline riding north-westwards over the gneissic basement and coarse clastic sediments along the West Islay Shear Belt (from Fiches and Maltman 1984):
2.5.2.1 Primary Structures in Islay and Colonsay:

In Islay, Appin and Argyll Group rocks are emplaced over immature feldspathic sandstones, the Colonsay and Bowmore Groups, along a tectonic contact or slide, the Loch Skerrols "Thrust". Correlations of the Bowmore Group with the Moine (Roberts 1974), the Torridonian (Cunningham-Craig et al. 1911), and the Crinan Grit (Fitches and Maitman 1984) have been made. The Bowmore and Colonsay Groups were originally correlated with the Torridonian, and appear on the British Geological Survey maps as such, due to their resting unconformably on high grade basement gneiss mapped as Lewisian. There are, however, lithological and geochemical differences between these rocks and both the Torridonian and the Moine leading Bentley et al. (1988) and Marcantonio et al. (1988) to regard them as an entirely separate stratigraphic unit or suspect terrain.

The Loch Skerrols "Thrust" has tended to be equated with the Moine Thrust Zone in the North West Scottish Highlands (eg Dewey and Pankhurst 1970). However, Fitches and Maltman (1984) showed that the Loch Skerrols "Thrust" was actually a shear zone whose fabric was continuous with the primary axial planar cleavage already discussed, and that the shear zone was, in fact, a slide (sensu Bailey 1922) emplacing younger rock onto older. Further, Fitches and Maltman showed that shear zones, tectonic breaks and fabrics formed during ductile deformation are present at structural levels below the Loch Skerrols Shear Zone; the whole of the west of Islay is a shear belt (referred to in this thesis as the West Islay Shear Belt) and its base is not exposed. All the fabrics and slides associated with this shear belt are continuous with the primary fanning axial planar cleavage developed in the Islay Anticline and on the mainland. Thus, while the rocks of Western Islay were thought to mark the foreland to the Orthotectonic or Metamorphic Caledonides, it is now clear that they are, in fact part of the Caledonian metamorphic belt.

Fitches and Maltman recognised a total of four deformational phases on Colonsay and Islay, two of which, the D₂, and D₃ deformations make up the equivalent on Islay and Colonsay to the Dalradian primary (D₁-D₂) deformation (table 2.1). The D₁ of Fitches and Maltman (1984) is seen developed locally as an alignment of sheet silicates and flattened detrital grains in the Bowmore and Colonsay Groups, usually parallel to bedding. The D₂ phase is the formation and emplacement of the major structures in Colonsay and Islay including the Islay Anticline and the West Islay Shear Belt. D₃ is a phase of open cylindrical folding.
Table 2.1 Correlation between deformational episodes recognised in different parts of the Scottish Dalradian

<table>
<thead>
<tr>
<th>Colonsay and Islay</th>
<th>Knapdale (Roberts 1974)</th>
<th>West-Central Highlands (Roberts and Treagus 1979)</th>
<th>Central-Southern Highlands (Harris et al. 1976, Harte et al. 1984)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D₂</td>
<td>B₁</td>
<td>D₁</td>
<td>D₁</td>
</tr>
<tr>
<td>D₃</td>
<td>B₂ₐ</td>
<td>D₂</td>
<td>D₂</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>D₃</td>
</tr>
<tr>
<td>D₄</td>
<td>B₂₉</td>
<td>D₃</td>
<td>D₄</td>
</tr>
</tbody>
</table>
of the same sense, vergence and geometry as $D_2$ modifying the $D_2$ structures on Islay, while controlling the outcrop patterns on Colonsay. Thus the dominant phase of deformation was the $D_2$ phase. Fitches and Maitman described increasing strain at lower structural levels including rootless North-West verging sheath folds, and tectonically modified sedimentary contacts. All these features imply that strain rates were at their highest at lowest structural levels, at the base of the napped pile represented by the Dalradian Supergroup and the Bowmore and Colonsay Groups.

Thus the primary folding and deformation on Islay was dominated by north-west-directed shearing accompanied by inclined tight to isoclinal folding with most of the strain taken up at the lowest structural levels. The individual shear zones nucleated on tectonic weaknesses, mainly sedimentary contacts modifying these as slides. The Bowmore and Colonsay Groups form the shear carpet along which the Islay Anticline rode as it was emplaced. Fig. 2.20 shows the structural relationships described by Fitches and Maltman.

The ductile nature of Loch Skerrols Shear Belt deformation is contrasted with the brittle nature of Moine Thrust Zone deformation. While biotite fabrics are developed at Kilchiaran bay (grid ref. NR 202601; Fig. 2.21) the temperatures of the rocks during Moine Thrust emplacement were much lower (Johnson et al. 1985) being barely high enough to develop chlorite zone mineralogy. In addition, movement on the Moine Thrust occurred at ca. 440 Ma (Kelley 1987) while the Dalradian primary deformation and, by implication, movement on the West Islay Shear Belt occurred about 80-100 Ma earlier (this thesis: chapter 6). Equating these two tectonic belts, different as they are in style and timing, clearly defies reality and observation.

### 2.5.2.2 Primary Structures in Knapdale:

To the south-east of the Islay Anticline is the Loch Awe Syncline, an upward-facing compound open to moderately tight fold, followed to the south-east by the isoclinal Ardrishaig Anticline, the root fold to the Tay Nappe. Roberts (1974), in his detailed study of the South West Highlands structures, divided the primary phase of deformation into three episodes, based on his own observations and those of Voll (1960). These phases were:

1. the $B_1$ deformation.

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Fig 2.21 Photomicrograph of 86-38, a biotite-bearing sheared grit from Kilchiaran Bay, South West Islay: the shearing is associated with movement along the West Islay Shear Belt, and the presence of biotite in this fabric indicates the temperatures of the rocks at the time of shearing.
2. the \( B_{2a} \) deformation,
3. the \( B_{1}B_{1} \) deformation.

The \( B_{1} \) deformation gave rise to the major folds in the area which have the fanning axial planar cleavage already described. A stretching lineation is developed on this fabric, pitching steeply, perpendicular to the strike of the fabric. In both Islay and Ardrishaig Anticlines, the axial planar fabric is parallel to the bedding and is defined by a strong alignment of sheet silicates in sediments and by sheet silicates and amphiboles in sheared intrusive and extrusive mafic rocks (this thesis section 3.4, Borradaile 1973). In the Ardrishaig Anticline, this fabric dips steeply to the north-west, forming the Knapdale Steep Belt. Between the axial traces of the Aberfoyle and Ardrishaig Anticlines, the stratigraphy is inverted, giving the Loch Tay Inversion.

The \( B_{2a} \) deformation has the same vergence, geometry and facing as \( B_{1} \) folds, as well as a similar stretching lineation developed on \( B_{2a} \) axial planar cleavages. This led Voll (1960) to label the \( B_{2a} \) deformation as a "symmetry constant continuation" of \( B_{1} \). Roberts (1974, p.104) described complex relationships between \( B_{1} \), earlier \( B_{2a} \), and later \( B_{2a} \) folding with late \( B_{2a} \) folds refolding both \( B_{1} \) and earlier \( B_{2a} \) folds, drawing the conclusion that deformation acted as a continuum, rather than as separate events, similar folds forming in a given packet of rock up to three times depending on the intensity of strain. This implies that the same regional stress field was in force at the time of \( B_{1} \) and \( B_{2a} \) deformation. A study and model of the trends of \( B_{1} \) and \( B_{2a} \) minor folds by Roberts and Sanderson (1973) showed that the strain increases with depth, so that, as was seen on Islay and Colonsay by Fitches and Maltman (1984), lower structural level rocks are more deformed than higher structural level rocks.

Roberts (1974) showed that the earlier \( B_{2a} \) folds form throughout the area, while the later \( B_{2a} \) folding was restricted to the Loch Tay Inversion, particularly the Southern Highland Group. The earlier \( B_{2a} \) fabric is a penetrative strain-slip fabric while the later \( B_{2a} \) fabrics vary between a crenulation cleavage and a chevron folding, depending on the degree of deformation. \( B_{1} \) and \( B_{2a} \) minor folds show normal assymmetry with respect to the closure of the major fold to which they are parasitic (Fig. 2.22).

The \( B_{1}B_{1} \) folding is developed locally in very highly deformed lithologies as moderate to open flexures of \( B_{1} \) and \( B_{2a} \) cleavage, with fold axes trending in a
Fig. 2.22 Geometrical relationships between $B_1$ and $B_2$, minor structures and the equivalent major fold (Ardrishaig Anticline) (from Roberts 1974):

Fig. 2.23 Simplified cross-section of the Loch Tay Inversion: this is bounded by the traces of the Ardrishaig and Aberfoyle Anticlines to the north-west and south-east respectively, between which the stratigraphy is inverted. The later ($B_{d4}$ or $D_4$) Cowal Antiform is defined by the Tarbert Monoform and the Highland Border Downbend (after Roberts 1974)
north-west to south-east direction, and without an axial planar cleavage. According to Roberts (1974), the B1B_1 folds formed as a result of north-east to south-west compression, this compression being localised and a response to the locally biaxial B_2a strain (Roberts and Sanderson 1973).

To summarise, the primary Dalradian deformation resulted in large scale nappe formation and transport, with at least three generations of folding present. The geometrical congruence of the first two generations implies that they occurred under the same regional stress field, probably as a continuum of deformation, rather than as discrete events.

There are clear similarities between the folding on Islay and that on the mainland, with a major, large scale phase of isoclinal folding of bedding, followed by later phases of folding with geometry similar to that of the first folds formed. Thus the B_1 of Roberts corresponds to the D_2 of Fitches and Maltman, and the B_2a of Roberts corresponds to the D_3 of Fitches and Maltman. It must be stressed that this correspondence is drawn mainly on structural style and do not necessarily imply equivalence in timing, although the D_2 of Fitches and Maltman and the B_1 of Roberts were almost certainly simultaneous, because their respective fabrics are continuous with one another. If this is so, the B_2a and D_3 folding were also roughly simultaneous, and probably very close in time to B_1 and D_2. The relationships between the fold phases as numbered on Islay and Colonsay, and on the mainland are summarised on table 2.1. However the major contrast between the deformational histories of Islay and Colonsay, and Knapdale and Tayvallich, is the presence of deformation occurring prior to the Tay Nappe-related folding on Islay and Colonsay, the D_1 of Fitches and Maltman (1984). Bentley et al (1988) suggest that the early deformation on Islay and Colonsay occurred prior to 600 Ma. The possible role of this early deformation in the metamorphic evolution of the South West Highlands is discussed further in 7.3.2.

2.5.3 The Secondary Deformation:

The later phases of deformation modified the geometry of folds emplaced during the primary deformation. The fold axes of the later deformation folds have Caledonoid north east-south west trends but the folding is concentrated in the lower structural level rocks in the Loch Tay Inversion and only rarely developed
at the higher levels around the Loch Awe Syncline. This section deals mainly with
the regional scale geometry of the later deformation and is based mainly on
Roberts (1974). Microtextures and microfabrics associated with the secondary
deformation are considered in chapter four. At this stage, no
comparisons are made with other parts of the Dalradian, these comparisons are
made in section 2.6 below.

According to Roberts (1974), the secondary deformation resulted in
steepening of the root of the Tay Nappe (the Ardrishaig Anticline) forming the
Knapdale Steep Belt. To the south-east, the crown of the arched Tay Nappe was
flattened into the Cowal Flat Belt such that it was folded from a steep attitude at
the Steep Belt into a flat attitude about the Tarbert Monoform. Further to the
south-east, another monoformal fold, the Highland Border Downbend, brought
the nose of the Tay Nappe downward relative to the Flat Belt giving rise to the
Highland Border Steep Belt. The two monoforms and the Flat Belt form a
compound fold, the Cowal Antiform (Fig. 2.23).

My own field observation of the coast between Tarbert and Skipness (Fig.
2.24) is broadly consistent with this view, except that the Cowal Flat Belt and
Highland Border Downbend are poorly defined in the South West Highlands.
The primary axial planar cleavage, and the bedding have a flat-lying attitude to
the south-east of the Tarbert Monoform and these steepen further to the
south-east, but there does not seem to be an abrupt change in dip, nor a zone
where monoformal minor folds are present. The Highland Border Downbend and
the Cowal Flat Belt are combined to give a gentle arching of the bedding and
primary axial planar cleavage, the Cowal Antiform, steepening to the south-east
rather than a well-defined monoform. Near Tarbert, minor folds of the axial
planar cleavage show asymmetry with closures towards the north-west, while in
the centre of Northern Kintyre, the minor folds are M-shaped and symmetrical.
At Claonaig and Skipness, minor folds are not well developed.

The first, f5, stage of Roberts in the secondary deformation was restricted to
the centre of the Loch Tay inversion and developed as strain-slip cleavages axial
planar to south-east verging minor folds which therefore verge in an opposite
direction to the primary B₁ and B₂a minor folds. This would represent the first
stages in the steepening of the Knapdale Steep Belt, making the rocks which now
make up the Cowal Antiform drop down as the top of the steep belt rotates to the
North West.
Fig 2.24 Map of the Northern Kintyre coast between Tarbert and Claonaig showing cartoons of structural folding styles developed across the Cowal Antiform in this region: while the Tarbert Monotorm is well developed, the Highland Border Down bend is not, and is limited to a gentle arching of $S_1$, schistosity, and bedding.
The next, f6, stage of Roberts was due to a strong North West directed simple shear deformation resulting in the completion of the Tarbert Monoform and Knapdale Steep Belt. Minor folds are open monoforms to isoclines of the primary axial planar cleavage and bedding, the tightness of the folding increasing to a maximum at the Tarbert Monoform axis then decreasing again to the south-east of this fold. This phase of the secondary deformation had two conjugate sets of minor structures associated with it, the vergences of which point to a simple shearing and rotation deformation directed to the north-west and resulting in the steepening necessary to form the Knapdale Steep Belt and the Tarbert Monoform (Fig. 2.25).

Structures congruent to the Highland Border Downbend were formed during the f7 deformation. It has already been pointed out that these structures are not well developed in Northern Kintyre, but Roberts describes them as south-east verging monoformal folds which therefore form a mirror image of structures to the Tarbert Monoform. The f6 and f7 deformation phases are clearly closely related although Roberts suggests that the Highland Border Downbend started forming later than the Tarbert Monoform.

All the minor structures associated with the secondary deformation suggest that this was dominated by the formation of the Knapdale Steep Belt. The secondary deformation involved simple shear and resulted in rotation of the rocks forming the Knapdale Steep Belt such that rocks at higher levels were emplaced north-westward over rocks at lower levels. The Highland Border Downbend, where developed, might have formed as a result of north-west-directed compression tucking the nose of the Tay Nappe under the Cowal Flat Belt, or as a drape structure off an uplifted block (Harte et al. 1984). Thus the entire secondary deformation took place as a result of trans-Caledonian compression directed towards the north-west, but with local variations in the folds developed. The Tarbert Monoform reduces in intensity to the north-east while the intensity of the Highland Border Downbend increases. These and other differences in the structural development of the Dalradian between the South West Highlands and the Central Highlands are addressed in the next section.
Fig. 2.25 Possible development of the Knapdale Steep Belt by north west-directed simple shear, based on the vergence of minor folds (after Roberts 1974).

Fig. 2.26 Calculated strain rates of different minerals as a function of temperature: Quartz deforms far more rapidly than mafic minerals, and, to a lesser extent, feldspar, at a given temperature. Thus, mafic rock at a given temperature is far more rigid than pelitic rock (from Kuznir and Park 1986).
2.6 Comparisons Between the Deformational Histories in the South West and the Central Highlands:

While the deformation history in the South West Highlands is relatively straightforward and unequivocal, that in the Central Highlands is much more complex and, as a result, controversial (e.g., Bradbury 1985, 1986, Nell 1986). However, many basic similarities in the general geometries of major folds in the two areas are apparent, as well as many differences. The similarities may be thought to imply that, for example, the first, isoclinal folding deformation occurred simultaneously in both areas. There are, however, few a priori reasons why this should be so, and many good reasons why it may not be (as pointed out by Bradbury 1986, p. 727). Lithologies and metamorphic grade show great differences between the South West and the Central Highlands, and the response of a rock to stress depends critically on both temperature and composition (Kuznir and Park 1986: see also section 2.7). In addition, metamorphic reactions will probably weaken a rock, making it more susceptible to folding (Graham and England 1976, Rubie 1983). The presence of a fabric, taken as evidence for deformation, is also evidence for metamorphic reaction and recrystallisation.

Bradbury (1986) also makes the point that a given fabric and geometry may be diachronous. Dempster (1985) showed that the highest metamorphic temperatures were attained in the Central Highlands over a time span of 30 Ma over a relatively small area. Thus, diachronicity in metamorphism, and possibly deformation was present, due primarily to localised variation in rates of uplift. Dempster linked the variations in uplift rates to the deformational and folding histories, thus implying that these vary along and across strike. This section is designed to draw cautious comparisons and contrasts between the South West and Central Highlands, with a view to elucidating the fundamental controls on the deformation histories and ultimately the metamorphism.

Throughout the Dalradian, the gross geometry of the deformed crust is similar, consisting of two belts of steeply dipping cleavage and bedding: a steep zone in the north-west and the Highland Border Steep Belt (Harte et al. 1984, Mendum and Fettes 1985), in the south-east. The two steep belts separate an area of flat-lying cleavage and stratigraphically inverted bedding, the Cowal Flat Belt (Bradbury et al. 1979, Harris et al. 1976). In addition, structures verge to the north-west from the steep zone, usually riding on a tectonic discontinuity, or slide,
over older rocks, this slide being the Boundary Slide in the Central Highlands and the Loch Skerrols Shear Zone in the South West Highlands. These areas in the Dalradian form part of the larger zone of north-westerly vergence forming the northern half of the Scottish Caledonides (eg Baker 1987), the Tay Nappe forming an exception to this trend by verging to the south-east.

The list of similarities between the two areas continues when considering the Tay Nappe and its emplacement. The consensus is that the Tay Nappe started as a inclined tight to isoclinal fold (but see Treagus 1987) which was rotated into recumbency and transported to the South East by simple shear (Harris et al. 1976, Bradbury et al. 1979, but see Mendum and Fettes 1984). In addition, there is general agreement that the majority of the rocks now exposed as the lower limb of the Tay Nappe fold (Ardishaig and Aberfoyle/Ben Lui Anticlines- Shackleton 1958, Roberts 1974, Mendum and Fettes 1984) are inverted stratigraphically (but see Watkins 1984) and that this inversion was due to isoclinal folding. Deformation after the isoclinal folding increases in intensity in both areas as lower structural levels are exposed. Finally, there is general agreement over the status of post- nappe emplacement modification of the Tay Nappe with downbending of the nose of the Tay Nappe (Harris et al. 1976, Mendum and Fettes 1984) towards the end of the Grampian - Caledonian deformation.

The major differences arise when considering the steep zone in both areas as a potential root zone for the Tay Nappe. While in the South West Highlands, the Ardrisaig Anticline which forms the Knapdale Steep Belt is unequivocally a root zone for the Tay Nappe and probably roots in its turn under the moderately open, upward facing Loch Awe Syncline, the presence of such a root zone in the Central Highlands is highly equivocal and controversial (eg Roberts and Treagus 1979, Thomas 1979, Shackleton 1979). In the Central Highlands, the base of the Tay Nappe appears to be bent under the Cowal Flat Belt in the north-west, so that it dips steeply to the south-east giving the cleavage and bedding an attitude parallel to the north-west verging structures riding on the Boundary Slide (Fig. 2.19). Essentially, the changes in the Zone of Divergence are that, in the South West Highlands, this zone is open and relatively simple in geometry, while in the Central Highlands, it is very tightly folded and has very complex geometry.

While in the Central Highlands, the Highland Boundary Fault Zone is well-developed, in the South West, it is diffuse and not recognised on the WINCH geophysical profile (Hall 1985). Deformationally, the zone of divergence in the

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South West is a moderately open syncline while in the Central Highlands, the folding is very tight and the stratigraphy is attenuated greatly (Roberts 1979 Treagus 1987). The Highland Border Steep Belt is well defined in the Central and Eastern Highlands where the Highland Boundary Fault is also well defined while in the South West, both Fault and Steep Belt are diffuse. The folding is also, of course, far more modified by later deformation in the Central Highlands than in the South West so the controversy concerning the existence or otherwise of a root zone to the Dalradian nappes is hardly surprising.

In summary, the major contrasts in the patterns of deformation between the South West Highlands and the Central Highlands are as follows:

1. the Zone of Divergence in the south-west is a simple, upward facing, moderately open syncline, while it is a complex structure with isoclinal folding and attenuated stratigraphy, having a north-westerly vergence.
2. The Highland Border Downbend and Highland Boundary Fault are diffuse and ill-defined in the south-west, but well developed to the north-east. In contrast, the Tarbert Monoform is well developed in the south-west, but dies out to the north-east.

All these contrasts are as a result of changes that occur across the trace of the Cruachan Line. The following section considers the possible controls of nucleation, emplacement and geometry of the large scale structures in the South West Highlands, together with their mechanisms of formation and evolution.

2.7 The Deformational History; Controls on the Evolution of Structures:

In this chapter so far, the depositional history of the Dalradian has been reviewed along with the geometry of the folds produced by Caledonian deformation. Contrasts in the depositional history between the South West and Central Highlands have been highlighted, along with the influences that these contrasts might have on the deformational histories of both areas. It is the aim of this section to develop the theme of controls on deformation in more detail, in particular, the influences on strain rates, intensities of deformation and the nucleation and growth of folds.

The main premise on which this section is based is that under a given stress, a weak medium will deform further and at a faster strain rate than a stronger
medium. An implicit premise is that stress was approximately homogeneous throughout the area. Clearly, stress concentrations can and will occur in a deforming metamorphic belt, but I feel that these variations would not be great enough in a belt such as the Dalradian, where ductile styles of deformation were dominant, to explain fully the contrasts in the patterns of deformation discussed above. Dalradian deformation is dominated either by folds, or by shearing. However, homogeneous stress in a heterogeneous medium will cause heterogeneous strain. The response of a rock to stress depends on its rheological properties, which in turn depend on temperature and composition.

Kuznir and Park (1986) have investigated the influences of temperature and mineralogy on the mechanical properties of rocks undergoing ductile strain. Some of their results are presented in Fig. 2.26, which is a plot of the calculated strain rates of a number of different minerals as a function of temperature. The curves are calculated from experimental data, but involve extrapolation from experimental conditions. The graph shows that, under given differential stress and pH$_2$O conditions, the strain rate of a mineral is very strongly temperature dependent, and strain rates vary very widely between minerals. In metasediments, quartz is the dominant phase modally, with sheet silicates also abundant, while in metabasic rocks, amphiboles and feldspar are dominant. No curves are shown for amphiboles, but all other mafic phases shown (pyroxenes and olivines) have strain rates several orders of magnitude lower than quartz at temperatures of about 400-500 °C, while feldspar has estimated strain rates about four orders of magnitude lower than quartz. Thus, at a given temperature and stress, a metasedimentary rock will probably deform between four and eight orders of magnitude faster than a rock made of feldspar and amphibole. Although data are lacking for sheet silicates, it is reasonable to suppose that these phases will have a low shear strength, due to their structure, suggesting that phyllitic lithologies will be among the weakest present in a varied sequence.

Because of the great lithological contrasts in the South-West Highlands, variations in strain measured by variations in intensities of deformation can be expected. So, it will be shown that there are correlations between deformation intensities and lithological types, and from these correlations, the structural evolution of the South-West Highlands will be reconstructed. The result will be to erect a structural model on which the construction of P-T-t histories can be based.
2.7.1 Controls on Deformation:

Although the Dalradian in the South West Highlands is lithologically diverse and complex, in general, mafic rocks are predominant in the Tayvallich and Northern Knapdale Areas, making up about 30% of the total stratigraphic thickness, while metasedimentary rocks predominate in areas to the north-west and south-east of the Loch Awe Syncline. In addition, phyllitic lithologies are present in the cores of the two major isoclinal folds. Thus, while mafic rocks are present in large quantities in the Loch Awe Syncline, marking the exposure of right-way-up stratigraphy, the Ardrishaig and Islay Anticlines are dominated by quartz-rich semi-pelites with, respectively, the Ardrishaig Phyllites and the Islay Limestones and Baharradail Phyllites in their fold cores. In addition, the Islay Anticline rides on the West Islay Shear Belt, which is dominated lithologically by metasediments, over an old, high-grade, gneissic basement. Thus, quartz-rich and phyllitic lithologies are found in the inclined to recumbent isoclines, while mafic rocks are concentrated in the moderately open Loch Awe Syncline and are far less abundant in the Loch Tay Inversion (Fig. 2.27).

There is also great variation in strain and the intensity of deformation in the South West Highlands. In addition to the varying geometries of the three major folds, strain and degree of deformation are higher at lower structural levels. In the Tay Nappe, the intensity of folding is greatest in the centre of the Loch Tay Inversion, and on Islay, the highest strains are seen in the West Islay Shear Belt. In the Loch Awe Syncline, however, the intensity of deformation is far lower and the large scale folding is more open in style than the two major anticlines. The Loch Awe Syncline was probably more open than it is now due to tightening during the secondary deformation. Thus, the degree of deformation was far greater in crust dominated by metasedimentary rock than in crust where mafic rock is abundant.

Within the two isoclines, weak, incompetent rock is preserved in fold cores while the limbs are more competent. Most models of fold nucleation and propagation treat rock as viscous or visco-elastic fluids (Hobbs et al. 1975, p. 201) and show that an inhomogeneous sequence undergoing layer-parallel shortening will only be folded if there is a large viscosity contrast between layers. If these models are realistic, they imply that the major reason why large scale deformation in the Dalradian was dominated by folding was due to lithological, hence...
Fig. 2.27 Map of the distribution of mafic rocks in Knapdale and Tayvallich. The Loch Tav Inversion marks a reduction in the proportion of mafic rock in the Dalradian (from Graham 1973).
rheological contrasts. The deformation in the more uniform Moine Supergroup appears to be dominated by sliding (not including the later, brittle Moine Thrust Belt), rather than folding. The isoclinal folds therefore probably nucleated in phyllitic horizons during Caledonian deformation. Although carbonates are present in Tayvallich, the preponderence of rigid mafic rocks and coarse grained sediments there probably precluded isoclinal folding.

Under a given stress, the rocks which undergo the greatest strains and displacements are the weakest and these rocks in the South West Highlands appear to be those dominated by metasediments. The crust which has been most intensely deformed is dominated by metasedimentary rock, while less intensely deformed crust has the most mafic rock. This correlation between lithology and deformational intensity is seen both on the outcrop scale and on the regional scale, with the shearing along sill margins around the Tayvallich area, recognised by Graham et al. (1983), (see also section 3.1), as well as the regional variation in structures suggested here. Thus the folding in the Dalradian displays much large scale competence control.

2.7.2 The Structural Evolution of the South West Highlands:

In the South West Highlands, there are three observations which allow modelling of the area's structural evolution:

1. the presence of an axial planar cleavage fanning across the Loch Awe Syncline,
2. the strong correlations between the dominant lithologies and the degree of deformation,
3. the increasing degree of deformation on the lower limbs of the isoclinal folds.

These three observations all point to the Loch Awe Syncline being a zone from which the two isoclines grew and propagated. The axial planar cleavages and stretching lineations all radiate outward from the core of the Loch Awe Syncline. The trends of all the major fold axes in the region show that compression acted in a north-west to south-east direction.

The ultimate source of the regional stress field which caused the Dalradian deformation is of course, not clear, though the thermal modelling described in
chapter 7 suggests that the under-thrusting of the basement gneiss wedge apparent
on the WINCH profile, and exposed structurally beneath the Loch Skerrols Shear
Belt, may have been the cause of the Dalradian deformation. Whatever its source,
the regional compression caused shortening of the sequence along a north-west to
south-east direction; the two isoclines would have nucleated in the phyllitic
horizons beneath the mafic rocks concentrated in the core of the Loch Awe
Syncline. These therefore behaved as a buffer against which compressive stress
acted. How the folds propagated out from the Loch Awe Syncline is not clear, but
there are two alternatives (Fig. 2.28):

1. straight-forward nucleation and growth of a fold with a steep to vertical axial
plane initially, followed by its gravitational collapse away from the Loch
Awe Syncline,
2. outward movement of rock along the now-inverted limbs as a result of
rotation of rock about axes near the Loch Awe Syncline and the two
isoclinal fold closures (cf. Bradbury et al. 1979; the folds propagating by
hinge-rolling.

The first alternative is similar to the models of Harris et al. (1976) and
Treagus (1987) who suggested that the precursor fold to the Tay Nappe, after its
formation by isoclinal folding as a close-to-upright fold, was emplaced by
south-eastward directed simple shear, and transported by an estimated 50 Km.
This alternative therefore requires that the Islay Anticline and Ardrishaig
Anticline spread apart after their growth and that the right-way-up limbs now
exposed in the Loch Awe Syncline be zones of major extensional deformation.
The second alternative explains the higher strain zones on the lower limbs of the
isoclines as being due to shearing of these limbs over the rock being fed beneath
the two isoclines, towards the Loch Awe Syncline. Thus, the folds are triggered by
the nucleation of folding in the phyllitic layers and grow by hinge rolling as a
result of pushing of the weaker, quartz rich crust against the stronger, mafic
rock-rich crust in the Loch Awe Syncline. The second alternative, hinge-rolling as
described here, does not require extension in the upper, right-way-up limbs of the
two isoclines (cf. fig. 1 of Shacketon 1979).

Although relatively little right-way-up rock is now exposed, enough is present
to show that the necessary extension (ca. 50 Km, Harris et al. 1976) has not
occurred, and that most of the deformation throughout the South West Highlands
is compressional. For these reasons, the second alternative, or rolling hinge model
for the growth and emplacement of the folds is preferred. As a result, apparent
Fig. 2.28 Two possible alternatives for the nucleation and propagation of the Tay Nappe: the Tay Nappe precursor fold is either initially upright and tight to isoclinial collapsing to the south-east under gravity, or it propagates as an inclined, tight to isoclinal fold by hinge-rolling at its closure and the Loch Awe Syncline. Both these models result in increased shearing and deformation at deeper structural levels.
large scale transport of the Tay Nappe can occur, but this would actually be due to relative movement of the Loch Tay Inversion over the lower level rocks.

Metamorphic pressures (Graham et al. 1983, this thesis, section 5.3) indicate at least 35 Km. of overburden during the primary deformation so that isoclines, as they form and propagate, would tend towards inclined to recumbent attitudes. This model therefore allows the Tay Nappe to form as an inclined to recumbent fold throughout its growth and emplacement. The alternative requires the up-doming of a large thickness of crust to an implausible extent. The only mechanism able to produce an inclined isocline involves rolling hinges. This mechanism explains the vergence of B_1 and B_2a minor structures by pushing of the core of the Tay Nappe towards the Loch Awe Syncline relative to its limbs. It will be shown in chapter 3 of this thesis that an initially inclined to recumbent Tay Nappe is most consistent with the geometry and position of metamorphic isograds.

During the secondary deformation, the Tayvallich and Loch Avich Lavas continued to play a buffering role rheologically and gravitationally. Roberts (1974) showed that this deformation was one in which monoformal folding occurred as a result of formation of the Cowal Antiform and Knapdale Steep Belt. While the Highland Boundary Fault precursor may have caused monoformal folding about the Highland Border Downbend (Harte et al. 1984), this lineament would have been absent in the South West Highlands, so the steepening was concentrated in the Knapdale Steep Belt; hence the presence of the Knapdale Steep Belt and its dying-out across the Cruachan Line.

Thus, north-west to south-east compression continued to operate after the primary deformation. Most of the secondary deformation was taken up in the Tarbert Monoform by the Ardrishaig Anticline being pushed north-westwards against the thick, rigid mass of the mafic rock to the north-west. The secondary deformation probably did not cause major uplift of the Cowal Flat Belt relative to the Loch Awe Syncline as the minor structures associated with the Knapdale Steep Belt formation (f6 and f6' of Roberts 1974) imply that shearing occurred horizontally to the north-west and steeply inclined to the south-east (this thesis, 2.5.3; Roberts 1974, p.115). Trans-Caledonoid compression continued as the nose of the Tay Nappe was arched over to the south-east.

Thus, deformation in the South West Highlands was due to a trans-Caledonoid stress field acting throughout the deformational history, causing
compression of the sequence and formation of large regional scale folds. The contrasts in deformational style between the South West and the Central Highlands was due largely to the strong contrasts in lithology and crustal composition between the two areas. The geometries of the folds developed in the South West Highlands were controlled by the competence of the crust over km length scales the variations in competence being due to the variation in the lithologies deposited and the depositional environment. Thus the geological history of the area has no vestige of a beginning....
CHAPTER 3
THE PRIMARY METAMORPHISM

"I don't want to cast the first stone, but you're making a big mistake..."

Gosciny and Uderzo, Asterix in Britain

In order to reconstruct the Pressure-Temperature-time (P-T-t) history of the metamorphic rocks of the South West Highlands, their mineralogy, petrology reaction history and assemblages need to be established. These aspects of the primary metamorphism will be described and discussed in this chapter.

Firstly, the mineral assemblages developed across the primary sequence will be described, along with the reactions relating these. Then, more detailed studies of grade related phase equilibria will be presented as composition-paragenesis diagrams. Metapelitic assemblages will be described in detail, their chemographic changes compared to those in metabasic assemblages. The compositional zoning patterns in garnets will be then described, along with the implications which these hold for the changes in P-T conditions during the prograde metamorphism.

Following this, the relationships between the primary metamorphism and deformation will be discussed. Here, the constraints available on the geometries of isograds and isotherms will be used to derive a qualitative 2-dimensional model of the thermal structure of the crust during primary metamorphism. This chapter is essentially qualitative; quantitative geothermobarometry estimates for primary metamorphism will be presented in chapter 6 while quantitative thermal models of primary metamorphism will be presented in chapter 9. Implications of the ideas developed in this chapter for other parts of the Dalradian will be discussed with particular reference to the attitude of the Tay Nappe during the early stages of its evolution and to the possible inversion of isograds in other parts of the Dalradian.
3.1 Assemblages and Reactions:

In this section, the state of knowledge of prograde metamorphism prior to this study will be reviewed, along with new information on pelitic assemblages and textures. Previous work on the fluid infiltration history will also be reviewed. Further details are found in Graham (1973), Harte and Graham (1975), Graham et al. (1983), and Greig (1985).

3.1.1 Assemblages:

Biotite Zone assemblages occupy the north-western part of the study area in Islay, Jura and Northern Knapdale and Tayvallich (Fig. 3.1) as well as the south-east in the south of Northern Kintyre. These two biotite zones are divided by the garnet zone which occurs in Central and Southern Knapdale, and the north of Northern Kintyre.

There are essentially four protolith types found in the north-western biotite zone. These are mafic volcanics and sills (Tayvallich Volcanics), carbonates (Tayvallich Limestones), coarse, clastic sediments (Crinan Grits), and carbonaceous phyllites (Ardrishaig/Craignish Phyllites).

Mafic rocks have two suites of mineral assemblages in the biotite zone; a hydrous suite and a carbonate-bearing suite. The hydrous assemblages are

\[
\text{act + ab + ep/zo + qz ± stilp ± bi ± sph}
\]

(see table 3.1 for abbreviations)

At higher grades, assemblages are

\[
\text{act ± hbl + ab + ep/zo + qz ± stilp ± bi ± sph}
\]

The hydrous suite of assemblages are seen in the centres of sills and are usually undeformed, often preserving relict igneous textures.

The carbonate-bearing assemblages are of several types, typified by the following:
Fig. 3.1 Map of the South West Highlands showing the distribution of metamorphic zones: this distribution is **not** the same as that in the map of Fettes et al. 1979.

Fig. 3.3 Zonation of metabasic assemblages in sills in the biotite zone: carbonate- and chlorite-rich assemblages overprint hydrous assemblages preserved in sill centres (from Graham et al. 1983).
Table 3.1 Abbreviations for minerals used in the text:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Abbreviation</th>
<th>Mineral</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>phengite</td>
<td>pheng</td>
<td>biotite</td>
<td>bi</td>
</tr>
<tr>
<td>chlorite</td>
<td>chl</td>
<td>quartz</td>
<td>qz</td>
</tr>
<tr>
<td>albite</td>
<td>ab</td>
<td>amphibole</td>
<td>amp</td>
</tr>
<tr>
<td>actinolite</td>
<td>act</td>
<td>hornblende</td>
<td>hbl</td>
</tr>
<tr>
<td>sphene</td>
<td>sph</td>
<td>rutile</td>
<td>rut</td>
</tr>
<tr>
<td>calcite</td>
<td>cc</td>
<td>dolomite</td>
<td>dol</td>
</tr>
<tr>
<td>ilmenite</td>
<td>ilm</td>
<td>magnetite</td>
<td>mag</td>
</tr>
<tr>
<td>tourmaline</td>
<td>tourm</td>
<td>garnet</td>
<td>gt</td>
</tr>
</tbody>
</table>

Fig 3.2 $T$-$X$-$CO_2$ plot for the reactions recognised as occurring in the biotite zone mafic assemblages by Graham et al. (1983): carbonate-chlorite-bearing assemblages are stabilised by increasing $X$-$CO_2$ of the fluid, so that biotite and amphibole growth are inhibited (from Graham et al., 1983).
(i) cc + act ± hbl + ab + ep/zo + qz ± stilp ± bi ± sph
(ii) chl + cc + ab + qz + ep/zo + pheng ± bi ± sph
(iii) chl + cc + ab + qz + pheng + rut ± bi
(iv) chl + dol-ank + pheng + rut

These assemblages define a zonation with increasing XCO₂ (= CO₂/(H₂O + CO₂) in the fluid), with the modal chlorite and carbonate increasing from the centres to the margins of sills and lava flows. Graham et al (1983) divided these assemblages into type I (amph + ep-bearing, cc-absent), type II (amph + ep + cc-bearing) and type III (cc + chl-bearing, amph + ep-absent). The type III assemblages are, in turn divided into (a) bi + sp + cc-bearing, (b) bi + rut + cc-bearing and (c) pheng + dol + rut-bearing parageneses (Fig. 3.3).

Carbonates are confined to the Tayvallich area. Typical assemblages are:

qz + cc + pheng + ab ± bi ± dol-ank ± tourm

In none of these assemblages do the phases sph + dol + bi + cc + pheng co-exist, although bi + cc + sph co-exist as do pheng + dol-ank. Biotite-bearing assemblages are limited at the lowest grades to intercalations between lava flows.

The Crinan Grits are also restricted to the lowest grade areas. Generally few metamorphic minerals are present due to their unreactive nature. Phengite and chlorite usually define a poor fabric wrapping coarse clastic quartz and feldspar.

The Ardrishaig Phyllites are found in northern Knapdale. Typical assemblages are

pheng + chl + qz + cc ± bi + ab

In Islay, kyanite-bearing mica-phyllites are found at Port Ellen. In addition, Loch Skerrols Shear Belt-related biotite-bearing fabrics are present as far west as the Rhinns of Islay (see Fig. 2.21).

In the Garnet Zone, lithologies are less varied and are dominated by semipelites (Erins Quartzites and Beinn Bheula Schists) with thin volcaniclastic (Green Beds) and carbonate (Loch Tay Limestone) horizons at Tarbert. Garnet zone mafic assemblages are marked by the absence of primary carbonate and
stilpnomelane, and are typically:

\[ \text{hbl + chl + ep/zo + ab ± bi ± gt} \]

in relatively Fe-rich bulk compositions and

\[ \text{act + chl + ep/zo + ab + qz + sph} \]

in relatively Mg-rich bulk compositions.

As modal garnet increases with grade, the modal chlorite and epidote decreases.

Garnet zone metapelites are of three types: garnet-bearing, garnet-absent and epidote-bearing:

(i) \[ \text{qz + pheng + chl + ab + bi + gt + ores} \]

(ii) \[ \text{qz + pheng + chl ± bi + ab + ores} \]

(iii) \[ \text{qz + pheng + bi + ep + ores} \]

The epidote-bearing assemblages are usually garnet-absent. Despite having undergone pervasive secondary, retrograde metamorphism (chapter 4), they have little or no modal chlorite. They are restricted to the volcaniclastic Green Bed horizons at Tarbert and Northern Kintyre. Carbonates in the garnet zone were studied in detail by Graham et al (1983) and Greig (1985).

3.1.2 Reactions:

Mafic assemblages are hydrated throughout the area, but are more so at lower grades. The protoliths to these assemblages, being basic igneous rocks would presumably have been dry, so the prograde metamorphism would have involved major hydration. However, because high grade assemblages are less hydrated than low grade assemblages, the reactions relating these involve dehydration. As will be shown subsequently, dehydration of initially very water-rich mafic assemblages over a regional scale will give rise to fluids which continue to be reactive at higher levels in the crust. This is reinforced by similar phenomena in pelites.
The biotite zone mafic assemblage types are related by a series of carbonation reactions progressing from the sill centres to the sill margins. The T-X-CO$_2$ positions of these reactions are illustrated on Fig. 3.2. In the system K$_2$O-CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O-CO$_2$ (KCMASHC), the hydrous type I assemblages are related to the carbonate-bearing types II and III assemblages by the reaction

\[
3\text{trem} + 2 \text{czo} + 8 \text{H}_2\text{O} + 10 \text{CO}_2 = 3 \text{chl} + 10 \text{cc} + 21 \text{qz} \quad (1)
\]

The type III cc-bi-rut assemblages are related to the pheng-dol-ank-sph assemblages by the following two reactions

\[
\text{bi} + \text{chl} + 8 \text{cc} + 8 \text{CO}_2 = \text{musc} + 8 \text{dol} + 3 \text{qz} + 4 \text{H}_2\text{O} \quad (2)
\]

\[
\text{sph} + \text{CO}_2 = \text{cc} + \text{rut} + \text{qz} \quad (3)
\]

Graham et al. (1983) in writing these reactions, calculated T-XCO$_2$ sections for the Schreinemaker's net of reactions concerned (Fig. 3.2). Essentially, progress of reactions (1) to (3) to the right as written is favoured by increasing XCO$_2$ in the fluid phase. The T-XCO$_2$ diagrams show that, at the P-T conditions concerned, the sill margins were infiltrated by a very water-rich fluid with X-CO$_2$ of about 0.002 to 0.005. Thus the degree of replacement of sill-centre type I assemblages by sill-margin type II and type III assemblages depends on the extent of infiltration of this fluid. The sill margins are sheared and this shearing has allowed the fluid into the sill margins preferentially while it left the sill centres unaffected allowing the type I assemblages to be preserved.

In biotite zone metasediments, reactions (2) and (3) were in operation relating biotite-bearing assemblages to later phengite-bearing mineralogy. It has already been pointed out that bi + cc + rut + sph + dol-ank + pheng never co-exist. This assemblage would buffer the fluid composition according to reactions (2) and (3). So the fluid phase composition was externally controlled. The metasediments have the same mineralogy as the type III metabasites so they were in equilibrium with the same fluid.

As grade increases, biotite and sphene become stable, representing the high temperature sides of reactions (2) and (3). The presence of biotite at the lowest grades shows that the whole area experienced biotite grade conditions of 0.0075.
metamorphism. However, biotite is only present in lithologies liable to have been protected from the infiltrating CO$_2$-bearing fluid. The protected lithologies were sediments intercalated between lava flows and the centres of sills. Prograde metamorphism therefore occurred as two episodes. The first was an early hydration, and the second was the CO$_2$-bearing fluid infiltration. This fluid may have been of similar composition throughout the biotite zone, differences in mineralogy being due to differences in temperature (see also Fig. 3.4).

The earlier type I metabasic assemblages became less hydrated with increasing grade. At lower grades, calcic amphibole is replaced by edenitic amphibole by the reaction

$$\text{stilp} + \text{act} + \text{ab} = \text{chl} + \text{hbl} + \text{qz} + \text{fluid} \quad (4)$$

This reaction defines an isograd splitting the biotite zone in two.

The garnet isograd reaction in mafic assemblages involves the progressive breakdown of stilpnomelane and epidote:

$$0.046 \text{stilp} + 0.289 \text{ep} + 0.17 \text{ab} = 0.082 \text{chl} + 0.318 \text{hbl} + 0.015 \text{gt}$$
$$+ 1.844 \text{qz} + 1.0 \text{H}_2\text{O} \quad (5)$$

This reaction was calculated by Graham (1973) using matrix algebra and real mineral compositions. Garnet first appears in Fe-rich bulk compositions and becomes progressively more Mg-rich with increasing grade by the breakdown of chlorite according to the reaction:

$$\text{Fe-rich chl} + \text{Fe-rich hbl} = \text{Mg-rich chl}$$
$$+ \text{Mg-rich hbl} + \text{gt} + \text{qz} + \text{fluid} \quad (6)$$

Graham et al. (1983) defined the garnet isograd by reaction (5).

In pelitic assemblages in the biotite zone, phengite is in equilibrium with chlorite (± biotite) + quartz. The continuous, progressive changes in these rocks are detailed below, but are due to the equilibrium

$$4 \text{cel} + \text{chl} = \text{musc} + 3 \text{phl} + 7 \text{qz} + 4 \text{fluid} \quad (7)$$
This reaction is continuous in biotite-bearing assemblages, but is the biotite isograd reaction in k-feldspar-absent pelites (Mather 1970, Miyashiro and Shido 1985). Garnet in metapelites is produced by reactions of the form

\[ \text{chl} + \text{pheng} + \text{qz} = \text{bi} + \text{gt} + \text{fluid} \]  

(Thompson 1976, Miyashiro and Shido 1985); the stochiometric coefficients depending largely on the chemistry of phengite. Reactions (7) and (8) and their effects on pelitic phase equilibria are discussed in more detail in section 3.2 and by Miyashiro and Shido (1985).

To summarise, the sequence of reactions in mafic and pelitic assemblages (as defined by changes in mineralogy across the area) consists of an early hydration episode, followed by overprinting of the resulting assemblages in the biotite zone by a CO2-bearing hydrous fluid. This overprinting was pervasive, resulting in fluid/rock ratios of locally greater than 10:1 (Graham et al. 1983, Greig 1985). With increasing grade, assemblages become progressively less hydrated.

3.1.3 Regional Fluid Infiltration:

Graham et al. (1983) calculated that time-integrated fluid-rock ratios were locally high at ca 10:1. An obvious source for this fluid would be regional dehydration reactions taking place in rocks now beneath the current biotite zone during the heating phase of their P-T-t trajectories.

The point should be made that these reactions would not have been identical to the isograd reactions listed above. Those reactions simply describe the trends of mineral chemistry developed between low and high grade assemblages which happen now to be exposed on the surface. To suggest that all the rocks now exposed actually went through these reactions would imply that their P-T-t paths followed the piezothermic array exposed by the progressive sequence. This of course is the view of regional metamorphism replaced by the models of England and Richardson (1977) which deduce that each "packet" of rock now on and below the surface followed its own P-T-t trajectory, largely independent of its surroundings.

It is clear, however, that, whatever the precise P-T-t paths followed by the
rocks in the area, large volumes of hydrous fluid would be released at depth by regional dehydration reactions. The fact that carbonate-bearing assemblages are present in the mafic rocks does indicate that the infiltrating fluid needs a CO$_2$ component, which would not be supplied by the devolatolisation of carbonate-absent assemblages. To find the source of this CO$_2$, Graham et al. (1983) report a set of carbon and oxygen isotope analyses of carbonate from pelitic and mafic sill margin assemblages. Fig. 3.5 summarises their data.

While carbon isotope values vary according to the country rock intruded by a sill, the oxygen isotope values show no such variation. Most noteworthy is the lack of significant difference between the carbon values of a sill margin and its country rock. Together with the between-country rock variations in carbon values, this shows that carbon isotopic values, hence the carbon in the carbonate within a sill, were locally derived. Volumetrically, oxygen from the CO$_2$ component would be insignificant due to the low XCO$_2$ of the fluid. This is because the H$_2$O-CO$_2$ fluid is oxygen-rich and carbon-poor; the carbon-13 in the rock is always internally buffered by the carbon in the rock, while the oxygen-18 is externally buffered. The source of the CO$_2$ in the Biotite zone is believed by Graham et al. (1983) to be either oxidised graphite, or sedimentary carbonate. The isotope data show therefore, that the hydrous component of the biotite zone fluid was derived externally to the Biotite zone, probably by regional prograde dehydration reactions in higher grade rocks at lower levels in the crust. The CO$_2$ component in this fluid would, however have been derived within the biotite zone, probably by oxidation of graphite.

3.2 Mineral Chemistry and Phase Equilibria:

In this section, mineral chemistry will be discussed as a qualitative indicator of metamorphic grade. The phase topological and chemical changes in two assemblage types will be considered and compared with one another. The assemblages are:

1. pelitic assemblages of quartz-albite-phengite-biotite-chlorite-garnet:
2. mafic assemblages of amphibole-albite-epidote-quartz-biotite-garnet:

The "progressive" changes in the chemistry of these assemblage types will be
*Fig. 3.4* Simplified version of Fig. 3.2: the arrows indicate the reaction pathways in the mafic assemblages caused by increasing \( X_{CO_2} \) as a result of infiltration of the \( CO_2 \)-bearing fluid through the sill margins in the greenschist facies (biotite zone) sills and increasing \( X_{H_2O} \) in the amphibolite facies (garnet zone) sills (From Graham et al. 1983).

\[
\delta^{13}C (M) = 0.079
\]

*Fig. 3.5* Simplified Lithostratigraphic map of Knapdale summarising stable isotope data from mafic assemblages and immediately adjacent country-rock:
Fig 3.6 Photomicrograph of 86-10, a phengite-biotite-chlorite-bearing quartzitic semi-pelite from the Lower Garnet Zone: the fabric in this assemblage is entirely planar and uncrenulated.
characterised, described and compared to give a qualitative assessment of metamorphic grade (without recourse to calculation of P-T conditions by geothermobarometry).

3.2.1 Principles:

Before discussing the results of the studies of mineral chemistry that have been made, the chemical changes that usually occur low to medium grade pelites, and the graphical representation of these changes, will be described in turn. The chemical changes can be written as substitution reactions whereby one cation, or group of cations in a phase exchanges for another cation, or group of cations in one or more other phases. The extent to which these substitution reactions change the phase chemistry is dependent on P-T conditions in suitable, buffering, assemblages, so the presence of similar assemblages metamorphosed under differing P-T conditions (to be quantified in chapter 5) allows the elucidation of the progress and direction of substitution reactions with changing metamorphic conditions, this being the main aim of this section.

It should become clear that the mineral assemblages developed in the South West Highlands during the primary metamorphism depend very strongly on bulk rock composition. As a result, a distinction will be drawn between the assemblage grade and the metamorphic grade. Differing bulk rock compositions metamorphosed under the same P-T conditions will give rise to different assemblages, which may be related to one another by a reaction. If the two assemblages are related by a chemical reaction, one of these assemblages will occur at higher grades than the other in identical bulk rock compositions. In two differing bulk rock compositions, the higher grade assemblage will grow at differing temperatures. Thus, the main aims of this section are the characterisation of grade-related chemical changes in the assemblages developed, and the elucidation of the effects of rock bulk chemistry on the development of assemblages with increasing grade. The second of these aims is the first step in working out the displacement of the critical reactions in P-T-composition (X) space, to be continued in chapter 5.
3.2.1.1 Substitutions:

In pelitic (KFMASH) assemblages, 2 compositional trends, or substitution reactions, can be used to characterise chemical change. The two composititional trends are:

1. The exchange between Fe and Mg (the FM exchange; Thompson 1957, 1976)
2. The Tschermak’s exchange (TS) of $M_2^+$Si for $2Al$;

where $M_2^+$ is usually Fe or Mg (Miyashiro and Shido 1985, Pattison 1987).

Using the vector notation of Thompson (1982), these two exchanges are written as follows:

1. $FeMg_{-1}$ for the FM exchange and
2. $(Mg,Fe)SiAl_{-2}$ for the TS exchange.

Each of the phases phengite, biotite and chlorite are solid solutions between at least two endmembers relateable to each other by the TS exchange. These endmembers are:

<table>
<thead>
<tr>
<th>Phengite</th>
<th>Muscovite</th>
<th>(musc) - $KAl_3Si_3O_{10}(OH)_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celadonite</td>
<td>(cel) - $KAl(Mg,Fe)Si_4O_{10}(OH)_2$</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>Eastonite</td>
<td>(east) - $KAl_2(Mg,Fe)<em>{2.5}Si</em>{2.5}O_{10}(OH)_2$</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>(phl) - $KAl(Mg,Fe)<em>3Si_3O</em>{10}(OH)_2$</td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>Antigorite</td>
<td>(antig) - $(Mg,Fe)<em>6Si_4O</em>{10}(OH)_8$</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>(clin) - $Mg_5Al_2Si_3O_{10}(OH)_8$</td>
<td></td>
</tr>
</tbody>
</table>

Phengite in equilibrium with biotite, chlorite and quartz obeys the following relation:

$$4\ cel + clin = musc + 3\ phl + 7\ qz + 4\ fluid$$  \hspace{1cm} (1)

Because this reaction has a high molar volume change, the composition of phengite in equilibrium with biotite, chlorite and quartz is stongly pressure-
dependent (e.g., Powell and Evans 1983). The studies of Miyashiro and Shido (1985) and Watkins (1987) ascribed changes in phengite chemistry dominantly to changes in temperature, disregarding or discounting pressure as a possible influence. In contrast, FM reactions have a small volume change, so they will be dominantly temperature dependent. As a result, use of both TS and FM reactions to characterise "progressive" metamorphism will lead to good first order constraints on P-T changes. This treatment is qualitative; quantitative calibrations of TS reactions in pelites are those of Powell and Evans (1983) and Bucher-Nurminen (1987); these are assessed and applied in chapter 5.

3.2.1.2 Composition-Paragenesis Diagrams:

Phase equilibria are represented in this section on triangular diagrams, on which changes in topology with grade give information on grade-related chemical change. The diagrams used normally in pelites are the AFM diagram of Thompson (1957) and the A'KF diagram of Eskola (1915) (see Miyashiro 1974, p.125). While the AFM diagram can represent changes due to both FM and TS vectors, it will be seen that TS affects phengites to the greatest extent. As the AFM diagram is a projection from muscovite, the "ubiquitous" phase, phengites cannot be represented on it. Although projections from epidote and k-feldspar can be made, the topologies resulting will not be rigorous as epidote is absent from most of the pelitic assemblages studied and k-feldspar is absent from all of these assemblages. In the first instance, therefore, the A'KF diagram is used to represent changes due to the TS exchange while the AFM diagram is used to represent changes due to the FM exchange.

Plotting parameters for the A'KF diagram are:

\[ A = \frac{Al_2O_3 - K_2O}{F/K+F = \frac{(FeO+MgO)}{(FeO+MgO+K_2O)} } \]

Defining \( A \) as \( Al_2O_3 - K_2O \) has the effect of plotting k-feldspar on the K apex and spreads the tie-line relationships out so that they are more clear.

The AFM plotting parameters are:

\[ A = \frac{(Al_2O_3-3K_2O)}{(Al_2O_3-3K_2O + FeO+MgO)} \]

\[ M/F+M = MgO/MgO+FeO \]
Mafic assemblages are plotted on the projection of Harte and Graham (1975). This projection is analogous to the Thompson (1957) projection, except it is concerned with compositions within the CaO-Al2O3-FeO-MgO (CAFM) tetrahedron projecting from epidote as the "ubiquitous" phase. Epidote, quartz and water are considered to be present to excess, while Na2O is only present in significant quantities in plagioclase. The variation of Na in amphiboles is due dominantly to the coupled edenite substitution, NaAlSi1−x. So, by subtracting Na2O from Al2O3 in the "A" plotting parameter, the variation in Na in amphiboles resulting from the Edenite exchange are largely accounted for.

3.2.2 Pelitic and Mafic Assemblages; Variation With Grade:

In pelites, grade-related chemical changes are measured and characterised by the chemistry of four phases: phengite, biotite, chlorite and garnet. While garnet and amphibole do not exchange chemically at low temperatures, but are replaced mineralogically during retrogression, phengites and chlorite can exchange chemically during retrograde metamorphism without recrystallisation. Therefore, comparisons will be drawn with previous detailed studies of amphibolites because these show few petrographic signs of retrogression. Because the sills in which these assemblages are found are highly competent, this is hardly surprising. Phase equilibria in mafic assemblages will be reviewed first, to provide evidence for the direction in which grade increases.

3.2.2.1 Mafic Assemblages; Variation With Grade:

Three sets of isogradien garnet zone assemblages are shown on the AFM projection of Harte and Graham (1975) in Fig. 3.7 (Fig. 7.5 of Graham 1973). It is clear that tie-lines are crossed in three-phase garnet-hornblende-chlorite assemblages. The projection as it stands rests on the assumption that Mn is equivalent to Fe in these assemblages. To test this assumption and the effects of its violation, a three-dimensional projection of CAFM compositions was made from epidote onto an AFM plane parallel to the CA edge of the CAFM tetrahedron. This plane defines a rectangle on which triangles with Mn at their apices are erected normal to it. One FeO-MgO-MnO (FMMn) triangle is present.
Fig. 3.7 AFM projection from epidote for mafic assemblages from Knapdale: crossing tie-lines imply either that Mn is behaving as an independent component or that discontinuous reactions occur between the assemblages (from Graham 1973).

Fig. 3.8 Projection of the same mafic assemblages as shown on Fig. 3.7 onto a three-dimensional AFMnM diagram: the surfaces resulting do not intersect, implying no discontinuous reactions and the independent behaviour of Mn.
for each of the three AFM phases considered, positioned at the appropriate "A" coordinate. Tie lines joining points for co-existing phases on the FMMn triangles define three-phase triangles which, if they intersect, define crossing tie line relationships. Plotting the assemblages of Fig.3.7 on this diagram shows that the three-phase triangles do not intersect and that Mn behaves as a separate component (Fig. 3.8). The garnet analyses are for garnet rims, because this phase shows marked compositional zoning.

With increase in grade, Mn contents decrease in garnet while Mg increases in hornblende and chlorite. These changes continue at least as far south as Tarbert; there are no mafic assemblages in Northern Kintyre. Grade therefore increases from the garnet isograd in Central Knapdale to the south-east and does not start falling until to the south-east of Tarbert.

### 3.2.2.2 Pelitic Assemblages; Progressive Changes in Chlorite, Biotite and Garnet:

Phengites will show some variability between assemblages due to the TS exchange. This has the result of moving the point of projection for the Thompson AFM diagram, so that variations due to the TS exchange cannot be represented rigorously. Phase topological variation due to the FM exchange may also be affected.

Fig. 3.9 shows an AFM (Thompson) projection of 2 three-phase (chl + bi + gt) assemblages, one from the garnet isograd, the other from West Loch Tarbert. Analyses from two-phase (bi + chl) assemblages from throughout the garnet zone of Knapdale are also shown. The lower grade assemblage, 77-101, has lower Mg/Fe ratios in all three phases than the higher grade assemblage, 86-8. Also, all three-phase assemblages have lower Mg/Fe ratios than all two-phase assemblages.

The possibility that the moving projection point may have an affect on phase topologies can be assessed by a diagram that disregards the TS exchange by not plotting Al contents. Such a diagram is the FeO-MgO-MnO (FMMn)diagram which has the added benefit of accounting for any possible de-coupling of Mn variation from Fe variation.

A projection from infinity parallel to the AFM plane used in the Thompson projection onto the Mg-Fe-Mn plane at "A"= 100 will be used here (Fig. 3.10). All three phases can be represented on this plane. Unlike the analogous diagram of Harte and Graham (1975), variations in the "A" parameter are insignificant -
Fig. 3.9 AFM projection from muscovite (J.B. Thompson 1957) for pelites from the garnet zone of Knapdale: the three-phase assemblages are Fe-richer than the two-phase assemblages, and the higher grade three-phase assemblages are richer in Mg.
Fig. 3.10 Construction of the Mg-Fe-Mn diagram by projection from infinity parallel to the AFM plane: the construction of this diagram is analogous to the diagram in Fig. 3.8 except that the variation in "A" in the phases shown is insignificant. As a result, chemical variations in chlorite, biotite, and garnet can be represented adequately on the Mg-Fe-Mn diagram. The progressive changes with grade in garnet-bearing pelites are shown: the plane joining garnet, biotite and chlorite rotates anticlockwise as viewed, as all three phases become Mg-richer, and garnet becomes Mn-poorer. Rock bulk chemistries defined by the two-phase tie-lines stabilise garnet when the three-phase plane intersects the two-phase line.
due to low variations due to the TS exchange. In addition to the Mg/Fe ratio variation already noted, lower grade three-phase assemblages have higher MnO in garnet and lower MnO in chlorite and biotite than higher grade three-phase assemblages (Fig. 3.11)

Because garnet is rich in MnO, its growth depletes biotite and chlorite in this component. Lower grade garnets have elevated MnO contents which are compensated for by lowered MnO contents in co-existing biotite and chlorite. As a result, the plane joining the phases together rotates anticlockwise when viewed parallel to increasing "A". The two phase lines are defined largely by bulk composition and garnet is stabilised when these and the three-phase plane intersect. The plane increases in width as the Mg/Fe ratios of biotite and chlorite increase. The biotite-garnet edge of the plane will also move away from the Fe-Al-Mn plane but the chlorite-garnet edge will lengthen as garnet tends to stay very Fe-rich.

3.2.2.3 Conclusions:

Grade changes in phases that are both mafic and aluminous (AFM phases) are measurable in terms of changing Mg/Fe ratios and Mn partitioning between phases in three-phase assemblages. The result is that 77-101 underwent lower metamorphic grades than 86-8.

The major conclusions, as far as grade-related chemical changes are concerned, are that garnet-bearing assemblages are Fe-richer than garnet-absent assemblages, at given metamorphic grades, and that, in both pelitic and mafic assemblages, Mg/Fe ratios increase with increasing metamorphic grade. The chemistry of the two-phase assemblages will not be fixed by the P-T conditions, but by bulk rock chemistry. The fact that garnet exists only in Fe-rich assemblages shows that, as concluded by several previous studies (Atherton 1970, A.B. Thompson 1976), its growth is favoured in Fe-rich bulk rock compositions. The very high Fe content of garnets in comparison to other AFM phases is the main reason for its growth being favoured by Fe-rich bulk rocks.

The other major conclusion is that it has been established by both mafic and pelitic assemblages that grade increases continuously from the Central Knapdale garnet isograd, to at least as far south-east as Tarbert.
**Fig. 3.11** Mg-Fe-Mn diagram for garnet-bearing and garnet-absent pelitic assemblages: the lower grade garnet-bearing assemblage, 77-101, has Mn-richer garnet than the higher grade garnet-bearing assemblage 86-8, so the biotite and chlorite are Mn-depleted. The high Mn contents in the biotite and chlorite in 86-8 suggest that garnet growth is favoured in Mn-rich bulk rock chemistries. The diagram also illustrates how garnet growth occurs first in Fe-rich rocks, as well as the increase in Mg contents with increasing grade.
3.2.3 Progressive Changes in Pelitic Phengites:

In the system KMASH, the TS exchange is buffered if phengite is in equilibrium with a minimum of three phases giving, with excess quartz and fluid, a phase-rule variance of one. Phengite + biotite + chlorite + quartz is present in nearly all the rocks considered, so these are buffering assemblages. Reactions relating these assemblages are of the form (Mather 1970, Miyashiro and Shido 1985):

\[ \text{Si-richer phengite} + \text{chlorite} = \text{Al-richer phengite} + \text{biotite} + \text{quartz} + \text{fluid} \quad (2) \]

Two stochiometrically balanced reactions following the form of (2) between the endmembers listed earlier are reaction (1) and:

\[ 3 \text{cel} + \text{antig} = 3\text{phl} + 7 \text{qz} + 4\text{H2O} \quad (3) \]

Since both of these reactions have celadonite on the left side of the reactions as written, their progress to the right will increase the muscovite component in the phengite solid solution. In addition, both reactions have biotite on the high entropy (dehydration) side. Thus, the Al content in phengite should increase with increasing grade.

For now, the composition-paragenesis diagram to be used in representing changes due to the TS exchange will be the A'KF diagram of Eskola - see also Miyashiro (1974; p. 125). Fig. 3.12 shows two A'KF diagrams for garnet-bearing and garnet-absent phengite-biotite-chlorite-bearing assemblages from the garnet zone. There are three garnet-absent assemblages; 86-10 is from Central Knapdale, 85-23 is from South Knapdale, and 87-10 is from Northern Kintyre. In these assemblages, the Al contents in phengites increase in the following order:

87-10 → 86-10 → 85-23

These assemblages therefore show clearly the expected trend of increasing Al content with increasing grade. In addition, biotite zone phengites are Si-richer than garnet-zone phengites (Fig. 3.13)
Fig. 3.12 AK'F diagrams for phengite-biotite-chlorite-bearing assemblages from the garnet zone of Knapdale:

(a) garnet-absent assemblages: Al contents in phengites increase with increasing grade; 85-23 is Al-richer than 86-10 and 85-10, which in turn are Al-richer than 87-10.

(b) garnet-bearing assemblages: phengites in 77-101 are very Al-rich, due probably to disequilibrium, while the phengites in 86-8 are slightly more Al-rich than those in the garnet-absent assemblages.
Fig. 3.13 A portion of the AK'F diagram showing phengite analyses from phengite-biotite-chlorite-bearing assemblages from the biotite zone, and garnet zone phengites for comparison: the biotite zone phengites are Si-richer than the garnet zone phengites.

Fig. 3.15 Phengite composition diagram of J.B. Thompson (1979, see also Miyashiro and Shido 1985): the fields predict the chemistry of phengites co-existing with the phases as labelled. Phengites co-existing with two phases plot along the lines separating the two fields concerned.
The phengites in 77-101 are Al-rich despite this assemblage being found near the garnet isograd of Central Knapdale. While Miyashiro and Shido showed that growth of garnet depletes phengites in celadonite component, such Al-enrichment is not seen in 86-8, even though the latter assemblage clearly underwent higher grades of metamorphism. 77-101 has a highly crenulated fabric; this crenulation has presumably affected the phengite chemistry. The phengites in 86-8 are slightly Al-richer than those in 85-23; this is due presumably to the Al-enrichment associated with garnet growth already referred to, and this assemblage undergoing higher grade metamorphism than the garnet-absent assemblages.

Because biotite, chlorite, and phengite are present in all the rocks described, one factor governing phase relations in these rocks will be the progress of reaction (1), the production and growth of biotite. The other major reaction that occurs in these assemblages is obviously the production and growth of garnet. The next subsection will consider these reactions in more detail.

3.2.4 The Growth and Stability of Biotite and Garnet in Medium Grade Pelites:

Mather (1970) showed that the first appearance of biotite occurs in bulk rock compositions with high Si/Al ratios. This implies that phengites in biotite-absent assemblages should be Al-richer than phengites in isogradic biotite-bearing assemblages. Mather (1970) did not, however, assess the influence of Fe/Mg ratio variations. Because biotite is an AFM phase, bulk rock Fe/Mg ratios will be important in fixing the temperature stability limit of biotite in a given "progressive" metamorphic sequence.

In this subsection, phengite will be treated as an AFM phase, because it has significant Fe and Mg contents, which can be expected to show variations with grade. Phengite-biotite-chlorite assemblages will therefore be represented on a projection onto the AFM plane from k-feldspar. This projection is non-rigourous in these assemblages because k-feldspar is almost always absent. Thus, crossing tie-line relationships must be interpreted with great caution. The reason for using this projection is the pragmatic one that it shows the variation between phases in a given assemblage the most clearly. In addition, variations in mineral chemistry due to the TS and FM exchanges can be seen on this diagram, resulting in clear representation of correlations between the two exchange reactions.
3.2.4.1 The Growth and Stability of Biotite:

In addition to the biotite-bearing assemblages already described, a biotite-absent assemblage from Central Knapdale, 85-25, has been studied. This assemblage is down-grade of 86-10, but still within the garnet zone. The mineral chemistry of this assemblage is compared with that of 86-10 in Fig. 3.14 and Fig. 3.16. The phengite in 85-25 is clearly more Al-rich than that in 86-10, despite experiencing lower grade metamorphism. It is also more Mg-rich. 85-23 has similar Al contents in its phengite, to 85-25, but is Mg-richer. Because biotite is absent from 85-25, mineral chemistry in this rock is not fixed by the P-T conditions of metamorphism, but by bulk rock chemistry. Thus, the Al/Si ratio in phengite will be a sensitive indicator of bulk rock Al/Si ratio, and the same applies for Mg/Fe ratios.

These trends are illustrated on Fig. 3.17, which is the empirically-derived phengite composition diagram of J.B. Thompson (1979; also discussed by Miyashiro and Shido 1985) (Fig. 3.15). On this diagram, the chemistry of phengite co-existing with biotite, chlorite, and k-feldspar is represented by the labelled fields, while the lines represent phengites co-existing with two other phases. The line separating the chlorite and biotite fields moves to Mg-richer compositions with increasing grade. On Fig. 3.17, arrays representing the phengite compositions in the assemblages discussed are shown, along with the inferred movement of the biotite-chlorite line. The diagram shows how 85-25 phengite is too Al- and Mg-rich to co-exist with biotite, while the other assemblages record increasing Al and Mg contents with increasing grade.

Thus, the trend noted by Mather (1970) is also displayed by these assemblages, with biotite growth being favoured in Si-rich bulk compositions. In addition, biotite growth is also shown to be favoured in Fe-rich bulk rocks, because the phengite in 86-10 is Fe-richer than that in 85-25. By observation, biotite is usually Fe- and Si-richer than either chlorite or phengite, so its growth at lowest metamorphic grades in Si-rich and Fe-rich assemblages is to be expected.

3.2.4.2 The Growth and Stability of Garnet:

A.B. Thompson (1976) showed that garnet grows as a result of the breakdown of chlorite and phengite according to a reaction of the form

\[
\text{chl} + \text{pheng} + qz = \text{bi} + \text{gt} + \text{H}_2\text{O}
\]

(4)
Fig. 3.14 (a) AK'F and (b) A'FM diagrams for two pelitic assemblages from the lower garnet zone: 85-25 is biotite-absent, and 86-10 is biotite-bearing; the phengites in 85-25 are Al- and Mg-richer than those in 86-10.
Fig. 3.16 A FM projections for garnet-absent pelites from the garnet zone of Knapdale: Mg contents in phengites increase with grade and correlate positively with Al contents.

Fig. 3.17 Phengite composition diagram with the topological variations with grade and assemblage derived in the text: the line separating chlorite and biotite moves to Al- and Mg- richer compositions with increasing grade so that 87-10 (a-a'), 86-10 (b-b'), and 85-23 (c-c') define the direction of increasing grade. Note the position of the biotite-absent assemblage 85-25, the phengites in this assemblage are Al- and Mg-richer than those in 86-10.
Because both biotite and garnet are Fe-richer than chlorite and phengite, the progress of this reaction to the high-entropy side is favoured by Fe-rich bulk compositions, as already intimated in the previous subsection. However, the influence of Al/Si ratios on the progress of this reaction is not so clear, because while biotite is Si-richer than chlorite and phengite, garnet is Si-poorer than chlorite. Miyashiro and Shido (1985) showed that reaction (4) is a linear combination of the biotite-producing reaction (1) and the reaction

\[
\text{bi} + \text{qz} = \text{cel} + \text{gt}
\]

As a result, the stoichiometry of reaction (4) depends on which of reactions (1) and (5) are more important in a given rock. Miyashiro and Shido (1985) suggest that this depends on the modal amount of chlorite in the rock, with chlorite-rich assemblages making (5) become more influential. As a result, it is difficult to make general statements about the effect of Al/Si ratios in bulk rocks on the growth of garnet. However the variation in Al/Si ratio in medium grade garnets is very small, so the major influence on garnet growth will be the bulk rock Mg/Fe ratio.

3.2.4.3 Summary and Conclusions:

The one major conclusion to be drawn from this subsection is that the growth of higher grade assemblages is favoured at a given metamorphic grade in bulk rocks that are Si- and Fe-enriched. This is indicated by the association between higher grade mineralogy, and Fe- and Si-rich mineral compositions.

These observations show that in pelites, ascribing stability relationships of assemblages solely to changes due to one or the other of the TS and FM exchanges will give rise to a misleading picture. Neither of the two substitutions discussed here should be treated in isolation; their direction and extent are strongly correlated, such that high Al contents are associated with high Mg contents, these in turn being associated with increasing metamorphic grades.

Fe/Mg ratios in garnet-absent pelitic assemblages will not be fixed by P-T conditions, while the phengite chemistries in the same assemblages will be. Thus, phengite chemistry is a very sensitive indicator of metamorphic grade. However, it should be noted that the TS exchange is strongly pressure-sensitive (chapter 5), so it is best used as a grade indicator in terrains where pressure has not varied to
too great an extent across the sequence concerned.

3.3 Compositional Zoning in Garnets

The last stages in the description of the prograde metamorphism are the qualitative characterisation of the senses of changing P-T conditions during the prograde event, that is, whether the crust was heating or cooling, and whether it was undergoing uplift or burial. These therefore represent the first stages in the construction of P-T-t paths for the area, having shown that metamorphism took place under biotite and garnet zone conditions and having described progressive mineralogical and chemical changes occurring in the assemblages of the sequence.

The mineral compositions preserved as the prograde sequence will, if in equilibrium, have preserved the maximum entropy (S\text{max}) P-T conditions as very small segments of the area’s P-T-t paths. Hence, no information is available on the changing P-T conditions prior to S\text{max}. However, the presence of compositional zoning in garnets leads to the proposition that only the rims of these are in equilibrium with the rest of the assemblages in which they lie. If the chemistry of these assemblages is fixed by P-T conditions, it follows that as one phase changes chemistry, so will the other phases in the assemblage. What also follows is the proposition that changing P-T conditions are recorded by the chemical zoning patterns. Spear and Selvestone (1983) and Holland and Richardson (1979) give examples of calculations of segments of P-T-t paths from zoned garnets and amphiboles respectively. As a result, qualitative changes in temperature will be derived from the zoning patterns.

The treatment in this section rests on the proposition that zoning in garnet is due to changes in the chemistry of the garnet itself, and of the phases with which it co-exists, during the growth of the garnet. The alternative is that post T\text{max} diffusion altered the original chemistry of the garnet. The patterns produced by growth zoning are well constrained by a number of fractional crystallisation and zone refining models (Harte and Henley 1966, Hollister 1966, Atherton 1968, Tracy 1982, Loomis 1984, 1986, and Loomis and Nimick 1982), all of which produce the same general trends. Diffusion data (Elphick et al. 1985, Loomis et al. 1985, Cygan and Lasaga 1985) and kinetic modelling, both theoretical (Lasaga 1983) and empirical (Yardley 1977, Dempster 1985a), show that diffusion of Fe
and Mg is only likely to be significant at temperatures of 600 °C or higher, conclusions that are confirmed by studies of progressive changes in zoning patterns in medium to high grade rocks (Booth 1984, Dempster 1985a)

3.3.1 Zoning Patterns:

Detailed zoning patterns have been constructed for grains in three assemblages. One of these (71-4) is an albite porphyroblast chlorite from South Bay, near Tarbert; the second, 86-8, is from West Loch Tarbert and is the highest grade primary assemblage studied in detail. The third (69-101) is a mafic assemblage from Tigh an Droighinn, Central Knapdale, and is therefore down-grade of the two pelitic assemblages. Detailed zoning patterns (from 30 spot analyses equally spaced across a 1 mm diameter grain) are shown in Fig. 3.18, for garnets from 71-4 and 69-102. Fe and Mg abundances both rise from core to rim while Mn defines the "classic" bell shaped profiles symptomatic of growth zoning. Ca remains more or less constant in 69-101 and drops near rims in 71-4. In none of these profiles do Fe and Mg show any zoning reversals near the rims. Due to the known metamorphic grade, this is not surprising. The Mn in 71-4 does show a slight reversal, due probably to the pervasive retrogression that has affected this assemblage (chapter 4).

Fig. 3.19(b) shows the zone profile from a garnet grain in 86-8. The Fe and Mn profiles are flat in the core, and near the rims, but change abruptly about half-way across the grain. Mg is enriched towards the rims while Ca is depleted.

The main features of interest in the profile from 86-8 are the discontinuities in Mn and Fe contents. While flattening of growth zone profiles at the rims would normally be associated with post-growth resetting by diffusion, the discontinuities in Mn and Fe abundances would require diffusion from lower to higher concentrations to occur, if the original profiles were like those in the other assemblages described above (Fig. 3.19(c)), directly contradicting Fick's Laws of diffusion. Fe-Mg-Mn diffusion can occur on 0.01-0.1 mm scales at the post-primary metamorphic cooling rates measured in the South West Highlands (5.4.2, 6.4.3), so diffusion may well have occurred in the garnets analysed, especially at the higher grades in the primary metamorphic sequence. However, the zoning pattern makes it unlikely that post-growth diffusion was the primary means of producing the observed profile.

The alternative is that two phases of garnet growth occurred in this assemblage at differing P-T conditions. During and after over-growth of the Fe-rich and Mn-poor rim, some Fe-Mn diffusion probably occurred across the interface
Fig. 3.18 Full garnet zoning profile from 71-4, a pelitic assemblage from South Bay, and a half profile from 69-101, a mafic assemblage from Tigh an Droighinn, in the lower garnet zone.
Fig. 3.19 (a) less detailed garnet zone profiles for garnets rimmed with chlorite from pelites from South Bay: the profiles have not been affected significantly in the garnet remnants.

(b) Zone profile from 86-8:

(c) Schematic development of the Fe zoning in 86-8: (i) growth of the core; (ii) overgrowth; (iii) diffusion of Fe between core and overgrowth, and between overgrowth and matrix.
between core and over-growth, and between the edge of the rim and the surrounding matrix, to produce the observed zone pattern (Fig. 3.19(c)). In the diffusion-rate calculations made in 5.4.3, the parameters used were for Mg-Fe coupled diffusion, and therefore suggest that Mg diffusion may also have occurred. However, Mg diffusion is difficult to resolve on the scale and detail available in this profile.

Though the textures in 86-8 make it impossible to categorically define times of garnet growth relative to structural history, the early stages of secondary metamorphism, suggested to have occurred during the D3 deformation of Harris et al. (1976), probably occurred at temperatures higher than 500 °C (5.5.1), and certainly at temperatures within the almandine-grossular stability field (4.3.1). Hence, the postulated overgrowth may well have occurred during D3, giving rise
to the possibility that the regional garnet zone in the South West Highlands may be poly-chronic, and that the drawing of "single-stage" garnet-in isograds (eg Watkins 1987, see also 3.5 and 3.6), may be mis-leading. The probable multi-stage growth of garnet also has implications for mineral chemistries, and for estimates of P-T conditions of metamorphism, since disequilibrium in the phases used for geothermobarometry may result. The phengite in 86-8 shows a greater compositional range than phengites in lower grade assemblages (3.2.2, 3.2.3), and therefore indicates disequilibrium. These possibilities are discussed further in 5.4.3.

3.3.2 AFM and Mn-F-M Relations:

The zoning patterns just described show that the four divalent cations - Fe, Mg, Mn, and Ca - vary along three different trends;

1. enrichment from core to rim (Mg and Fe)
2. enrichment from core to rim (Ca)
3. depletion from core to rim (Mn).

In addition, it has been shown in section 3.2, and is generally known, that Mg/Fe ratios are a sensitive grade indicator. In view of the aims of this section, elucidation of changing cation ratios will be of paramount importance. It has also been shown that Mn is capable of interfering with phase relations by acting independently of Fe. Again, variation in Mn will be important in a phase where it is so abundant.

Because of the antipathetic variation of Mg and Fe with Mn, it is tempting to conclude that these elements are linked. This conclusion is assessed in Fig.3.20 which shows $X_{Mg}$ and $X_{Fe}$ plotted against $X_{Mn}$; expressed as percentages. Although both diagrams show scatter, they both also show that Mg and Fe are strongly inversely correlated with Mn and suggest that Mn substitutes equally for Mg and Fe. This suggests that Mg/Fe ratio trends will be real and not a result of preferential substitution of Mn for one or the other of Fe or Mg.

To show variation in divalent cation abundances, triangular diagrams of Mg/Fe/Mn (M-F-Mn) and Ca-Fe-Mg (CFM) variations will be used. M-F-Mn diagrams for both pelitic and mafic garnets are shown on Fig. 3.21. The Mg/Fe increase from core to rim is shown clearly. This is also seen in CFM diagrams for
Fig. 3.20 (a) $X_{Mn}^{Mg}$ v. $X_{Mn}$ and (b) $X_{Fe}^{Mn}$ v. $X_{Mn}$ in garnets from Knapdale: the linear correlations imply that Mn substitutes equally for both Fe and Mg, and that Mg/Fe ratio variations are real trends, not an artifact of preferred substitution of Mn for one, or another, of these elements.
Fig. 3.21 Mg-Fe-Mn diagram for garnets from pelitic and mafic assemblages: the Mg/Fe ratios increase from core to rim implying that temperatures were increasing during garnet growth.
the two rocks (Fig. 3.22), with Ca abundances showing clear declines from core to rim in both assemblages. However, the range in variation in the mafic assemblage is far less than in the pelites. This is almost certainly due to the buffering of Ca by matrix phases such as hornblende and epidote. In pelitic assemblages, the plagioclase is very albitic and epidote is rare, normally only present in garnet-absent assemblages. To summarise, therefore, all garnets analysed show increasing Mg/Fe ratios and decreasing Mn and Ca abundances. These changes are independent of locality and mineral assemblage.

3.3.3 Equilibria Controlling Garnet Composition:

In the previous subsection, the changes in divalent cation abundances and ratios were described. It is clear that while Mn, Mg and Fe are linked closely, Ca behaves independently, so two equilibria for each assemblage will control the garnet chemistry. One of these equilibria will be written in the KFMASH system and will involve the FM exchange between co-existing phases. It will therefore be very sensitive to temperature. The observation that no major discontinuities (jumps, reversals etc.) are present can be taken to mean that no discontinuous reactions have been crossed during garnet growth (Tracy 1982, p. 361) and that the mineral assemblages now present were the assemblages with which the garnets were in equilibrium throughout their growth. So, in 69-101, growth occurred in equilibrium with the AFM phases hornblende and chlorite, and the CFM phases epidote and calcic amphibole. In pelites, garnet growth occurred in equilibrium with the AFM phases biotite and chlorite, while the grossular component was not buffered and is not therefore fixed by P-T conditions.

It was shown in 3.2 above that Mg/Fe ratios in both mafic and pelitic 3-AFM phase assemblages are strongly grade-dependent. In pelites, the AFM reaction controlling the growth of garnet is of the form (neglecting coefficients)

\[ \text{chl} + \text{musc} + \text{qz} = \text{bi} + \text{gt} + \text{fluid} \]

(section 3.2, reaction (5))

All these phases are present in garnet-bearing pelites and this reaction progresses to the right (dehydration and high entropy) hand side with increasing
Fig. 3.22 CFM diagram for garnets from (a) mafic, and (b) pelitic assemblages: Ca decreases from core to rim in all garnets.
temperature leading to increasing Mg/Fe ratios in co-existing biotite, chlorite, and garnet with increasing temperature (Thompson 1976). The assemblages in which the garnets analysed are found have been affected pervasively by secondary metamorphism, so they are no longer in equilibrium with the analysed garnet. However, both biotite and chlorite inclusions are present in secondary albite porphyroblasts. The assemblage buffering FM variation in garnet according to the above reaction therefore was similar to that in the above reaction. Thus, increasing Mg/Fe ratios in the garnet from core to rim suggest that temperature was increasing as the garnets grew. 86-8 garnets show similar trends of Mg-enrichment towards the rims but has not been overprinted by pervasive secondary metamorphism. The zoning patterns therefore indicate that temperatures were increasing during garnet growth.

In mafic assemblages, the continuous AFM reaction controlling garnet growth was of the form (neglecting coefficients)

\[
\text{Fe-chl} + \text{Fe-hbl} = \text{Mg-chl} + \text{Mg-hbl} + \text{gt} + \text{qz} + \text{fluid}
\]  

(\text{section 3.1 reaction (7)}).

Accounting for the complexities caused by the behaviour of Mn, this reaction also progresses to the right and causes increasing Mg/Fe ratios with increasing temperature. Again, the increasing Mg/Fe ratios in these garnets imply that the area was being heated when garnet growth occurred. The similarities in the zoning of three assemblages from three far-apart localities in the garnet zone suggest that garnet growth occurred while the temperature was increasing, and also that garnet growth throughout the area probably occurred at similar times. The zoning patterns also mirror the chemical changes with grade seen in assemblages throughout the garnet zone: Mg/Fe ratios increase with grade, hence temperature, in the garnets and in the assemblages, while Mn decreases with grade in the assemblages, and with the increasing temperature recorded in garnet zoning profiles.
3.4 The Timing of Growth of the Primary Assemblages Relative to Deformation:

In chapter 2, the deformational history of the South-West Highlands was described and it was shown that it can be divided into a primary major inclined to recumbent folding and nappe formation episode, the D\textsubscript{1}-D\textsubscript{2} deformation, followed by later, more localised monoformal folding, the B\textsubscript{a,b}, or D\textsubscript{4}, deformation. It was also suggested that the dominant primary metamorphic assemblages grew during the primary deformation (D\textsubscript{1}-D\textsubscript{2}) and that secondary and overprinting metamorphism occurred subsequently. Textural evidence will be presented linking prograde metamorphism to the D\textsubscript{1}-D\textsubscript{2} deformation in time and contrasts between this and the Central Highlands will be discussed.

In this section, the assemblages whose timing of growth is to be linked with the primary deformation are those assemblages which are dominant, or which are the most widely developed. Normally, the most widely developed assemblages are prograde, or they grew while the crust undergoing regional metamorphism was at temperatures close to the highest attained. In many metamorphic belts, secondary assemblages grew at lower temperatures than the primary assemblages and were therefore retrograde. However, it will be shown in chapter 5 that the early stages in the secondary metamorphism in the South West Highlands occurred at temperatures that were close to, and may have been locally higher than, the temperatures under which the primary assemblages grew. Thus, the assemblages in the South West Highlands are divided solely into early and late, the division being made in the first instance on textural grounds. The aim of this section therefore, is to ascertain the timing of growth of the primary assemblages relative to the deformational history, and it will be shown that, unlike the Central Highlands, the dominant assemblages in the South West Highlands grew during the primary, nappe-forming deformational event.

To show that the dominant metamorphic assemblages grew during the first deformational episode, the following criteria need to be met:

1. Minerals associated with the metamorphism grew in fabrics and alignments relateable directly to the deformation.
2. The deformation concerned has a fabric that is either undeformed, deformed by later fabrics or deforming bedding. This fabric must not deform another tectonic fabric.
3.4.1 Petrography:

Figs 3.23-3.27 are photomicrographs of a number of metabasic and metasedimentary assemblages collected from the biotite and garnet zones of Knapdale by myself, Dr. C.M. Graham and Dr. B. Harte. These all have planar fabrics as well as mineralogy associated with the prograde metamorphism. Fig. 3.23 and 3.24 show lowest grade biotite zone assemblages, 69-217BH, which is a cc + qz + pheng-bearing metacarbonate from the Tayvallich Peninsula, and 86-2 which is a sheared grit also from Tayvallich. The fabric in these rocks is refracted locally from metasedimentary to metabasic horizons and is continuous with metasedimentary fabrics axial planar to upright folds of bedding subsidiary to the D₁ Loch Awe Syncline.

Assemblages from near the garnet isograd are shown in Figs 3.6 and 3.25. These assemblages, 86-10 and 71-12, are pelitic with biotite and muscovite aligned in planar fabrics and one, 71-12, has garnets. These garnets do not have inclusion trails so their growth cannot be linked unequivocally to a specific deformation. However, the garnets do not post-tectonically overgrow any fabric, nor is there any crenulation of the fabric in this rock. There is evidence of limited post-tectonic growth of biotite as unaligned grains optically very similar to the aligned grains. It is clear that no primary metamorphism can be linked with any significant post-D₁ deformation in these assemblages.

86-10 is from the garnet zone and bears the assemblage qz + pl + pheng + bi + chl and also shows no sign of crenulation of a planar fabric. It was collected from Tigh an Droighinn. Other specimens from this locality have similar mineralogy and fabrics but these show monoformal microfolds in less competent horizons. So the highest temperature mineralogy is found in assemblages with dominantly planar, uncrenulated, fabrics, though the lack of good porphyroblast inclusion trail relationships means that these observations on their own are not sufficient to show that primary metamorphism occurred during D₁-D₂ deformation throughout the area in all assemblages.

The amphibolite assemblages in Fig. 3.26 and 3.27 are better evidence of syn-D₁-D₂ primary metamorphism, especially 70-86 which is from South Bay and contains hornblende and biotite defining a fabric crenulated by micro-monoforms. As in 71-12, biotite growth seems to have outlasted the fabric-forming
Fig. 3.23 Photomicrograph of 69-217BH, a carbonate-quartz-phengite-bearing assemblage from Tayvallich Peninsula, lower biotite zone; the fabric is planar and uncrenulated (ppl).
Fig. 3.24 Photomicrograph of 86-2, a quartz-phengite-chlorite-biotite-bearing pelitic assemblage from Tayvallich Peninsula, lower biotite zone: a well-developed planar shear fabric envelops clastic feldspar grains (ppt).
Fig. 3.25 Photomicrograph of 71-12, a quartz-phengite-biotite-chlorite-garnet-bearing metapelitic assemblage from Clachbreck, upper garnet zone: biotite and phengite define a planar fabric, but some biotite is unaligned growing between planes of schistosity. Growth of the garnet cannot be linked unequivocally to growth of the schistosity; however, the garnet also does not overgrow the fabric (ppl).
Fig 3.26 Photomicrograph of 70-86, an amphibole-biotite-albite-garnet-bearing mafic assemblage from South Bay, upper garnet zone. The schistosity is defined by amphiboles and is crenulated by monoformal microfolds; garnet inclusion trails are parallel to the uncrenulated schistosity (cpl).
Fig 3.27 Photomicrograph of 84-2, an amphibole-albite-garnet-chlorite-bearing mafic assemblage from Glen Achagragach Forest, upper garnet zone. The schistosity is defined by amphiboles and is crenulated; garnet inclusion trails are parallel to the uncrenulated schistosity (cpl).
deformation. Garnet inclusion trails are parallel to the hornblende-biotite fabric. In this rock, the highest grade mineralogy grew during the growth of the first fabric preserved. 84-2 shows garnets with curved inclusion trails. They therefore grew during a tectonically active period. The fabric in 70-86 is parallel to pelitic S1 fabrics axial planar to the Ardrishaig Anticline.

To summarise the petrographic evidence, the primary mineral assemblages always grow in fabrics that are either planar and do not cross cut any tectonic fabric, or are deformed by subsequent microfolding and crenulation. The fabrics in which the primary mineralogy is aligned are axial planar to folds of bedding and form the fanning cleavage associated with D1 or B1 deformation and folding. The primary assemblages must therefore have grown during the earliest preserved stages in the deformational history of the South West Highlands.

3.4.2 Conclusions and Implications:

It is clear from section 3.1 that metamorphism in the biotite zone consists of two assemblage-forming "events" which, from textural information are closely linked in time with each other and with metamorphism in the garnet zone. Earlier type I assemblages are overprinted by S1 fabrics axial planar to upright folds of bedding. Types II and III assemblages define these fabrics and are linked by the fluid phase to dehydration reactions in higher grade rocks below the present exposure surface. Equivalent dehydration reactions are seen at two isograds, the Stilp-Act = Hbl-Chl isograd and the Garnet isograd. Textures in the garnet zone assemblages show that these also grew during the primary deformation because their fabrics are axial planar to isoclinal major folds of bedding, parasitic to the Ardrishaig Anticline. Some pelites are garnet-bearing; growth of garnet in these rocks cannot be timed unequivocally but does not seem to be syn-tectonic to any significant post-D1-D2 deformation in these rocks.

The styles of deformation, as described in chapter 2 are very similar to styles described as D1-D2 in other parts of the Dalradian (Roberts 1974, Harris et al. 1976, Roberts and Treagus 1977, 1979). Limited "symmetry-constant continuation" (Roberts 1974) is seen folding S1 and more pervasive secondary deformation is seen in the South East of the area. It will be shown in chapter 4 that folding styles similar to the D3 of Harris et al. (1976) are preserved as inclusion trails in albite porphyroblasts and that later overprinting metamorphism
was taking place at this time. This is a major contrast with the Central Highlands where, the prograde metamorphic climax largely occurred during the $D_3$ deformation (Harte et al. 1984, Harte 1988).

Two major sets of implications of this conclusion are:

1. The crust in the South West Highlands started cooling earlier than in the Central Highlands. The radiometric age data to be discussed show that this cooling occurred earlier in absolute time than in the Central Highlands, as well as earlier relative to deformational histories (which are possibly diachronous).
2. The primary phase of folding resulted in high amplitude folds which are now inclined to recumbent. Because temperatures high enough to result in the growth of garnet were attained during this folding, the possibly rapid translation of large rock masses would have affected the thermal structure of the crust. What is clear is that metamorphism, deformation and fluid flow seem to be linked very closely. In view of the rheological weakening of rock during large scale mineral reaction (Rubie 1983), and fluid production (Graham and England, 1976) a series of feedback mechanisms linking factors kinetically favouring metamorphic reactions and rock deformation seems to have been in operation.

One implication is that metamorphic reaction and recrystallisation may be transient events punctuating the steady thermal and P-T-t evolution of the metamorphic belt. Thus, only during a relatively small proportion of a rock’s P-T-t path does mineral reaction occur. The crossing of the P-T-X locus of a reaction by a P-T-t path may not be sufficient on its own to bring about reaction, because of the activation energy barrier to reaction (e.g. Ridley 1985). Metamorphism will, however, occur if fluid infiltration and/or deformation occurs. Rocks are weakest at their highest temperatures (e.g. Kuznir and Park 1986) and further weakening will occur if fluids are present. Thus, the time of attainment of $(P-T)_{T_{\text{max}}}$ will be close to the time at which $(P-T)_{S_{\text{max}}}$ will be attained, and is therefore the most favourable time for the growth of dominant, primary assemblages in a given metamorphic belt.

### 3.5 Isograds, Isotherms and Tectonism:

In section 3.4, it was shown that prograde metamorphism occurred during primary deformation at an earlier time than in the rest of the Dalradian. In this section, and section 3.6, the position of isograds on the present day erosion
surface will be described. Then the syn-prograde metamorphism geometry of
isothermal surfaces and hence, the thermal structure of the crust will be derived
as the first, qualitative stage in the thermal modelling to be carried out in
chapter 7. The occurrence of prograde metamorphism during $D_1$-$D_2$ and the
probable isotherm geometry will enable the probable syn-$D_1$-$D_2$ geometry of the
Tay Nappe to be derived.

3.5.1 The Actinolite-to-Hornblende Isograd:

In section 3.1, it was demonstrated that two isograds can be drawn based on
metabasic mineral assemblages. The lower grade isograd is the breakdown of Act
(+ Stilp) to Hbl + Chl assemblages according to reaction (4).

Fig. 3.28 shows the exposures of this isograd in Northern Knapdale and
Tayvallich areas. The figure also shows the axes of the Tayvallich and Kilmory
Bay synclines. It is clear that these fold axes, bringing highest structural level rock
into exposure, coincide with the presence of the lowest grades of metamorphism.
The cross-section illustrates this relationship and the apparent folding of the
isograd surface resulting. Either there were very localised differences in
temperature, or the isograd surface has been folded. It is very unlikely that such a
small scale thermal anomaly would have persisted long enough to result in its
preservation as regional metamorphic mineralogy (see below, 3.6.1 and chapter 7).

The isograd surface would therefore have been smoother topographically but
still subparallel to bedding. Pressure estimates of prograde metamorphism
(chapter 5) suggest that the thickness of overburden at this time was similar
throughout the South West Highlands, but was greater in the south-east where
higher grade and deeper structural level rocks are exposed. The Ardrishaig
Anticline has therefore been uplifted relative to the Loch Awe Syncline after
folding (see chapter 2). This differential uplift has resulted in folding of the
actinolite-to-hornblende isograd subsequent to its formation, as well as tightening
of the Loch Awe Syncline. Evidence for late tightening of the Loch Awe Syncline
is found in the Carsaig area at grid ref. NR 727877. Here, $S_1$ cleavage axial planar
to a minor $F_1$ fold of bedding is deflected across bedding planes as a result of
strain-slip deformation. This can only have occurred post-$D_1$ because $S_1$ fabrics
are displaced.
Fig. 3.28 (a) Map of the biotite zone in Tayvallich and North Knapdale with traces of $D_1$ synclines and exposures of hornblende and actinolite-bearing mafic assemblages: note the close coincidence between the actinolite-bearing assemblages and the traces of the folds (after Graham 1973).

(b) Schematic cross-section through the Loch Awe Syncline showing the relationships of metamorphic grade in this area with structural depth: the isograd surface has probably been folded by post $D_1-D_2$ folding caused possibly by quicker uplift of the deeper structural level rocks to the north-west and south-east subsequent to primary
3.5.2 The Garnet Isograds:

Prior to this study, the garnet zone as defined by the first appearance of garnet in metabasic assemblages to the north and pelitic assemblages to the south was believed to occupy Central and Southern Knapdale, with lower grade rocks exposed to the south-east of Tarbert (Tilley 1925, Graham et al. 1983). Watkins (1983) speculated that this position for the isograd was suspect, and my own petrographic observation is consistent with this. 6 km across-strike downgrade of Tarbert, in Northern Kintyre, specimen 87-8 was collected. This is an albite-chlorite schist containing remnants of large almandine-grossular-rich garnets. The garnet zone can thus be seen to extend along the coast at least 6 km south-eastwards from Tarbert.

In section 3.2 above, it was shown that the highest grades of metamorphism are seen close to Tarbert. Suggesting that biotite zone rocks occur close to the higher grade garnet zone rocks near Tarbert implies that the temperature gradients during metamorphism were very steep, and may have been inverted. The possibilities for inverted metamorphic zonation at Tarbert and in other parts of the Dalradian is considered further in 3.6 below, but it will be shown here that basic observations of correlation between metamorphic grade and lithology and exposed structural depth predict that the position of the southern limit of the garnet zone at Tarbert must be suspect.

Fig. 3.29 shows Tayvallich-Knapdale-Kintyre cross-sections with D1 and other fold axes marked. The Graham et al. (1983) and Tilley (1925) isograds in Knapdale and Tarbert respectively are shown in the first cross-section. A garnet zone between these two lines is therefore confined to the stratigraphically inverted limb of the Knapdale Steep Belt, and the grade-structural depth correlation present in North Knapdale and Tayvallich is clearly violated to the south of Tarbert. The second cross-section shows the less well-constrained position of the southern garnet isograd in Northern Kintyre based on the locality of sample 87-8. The grade-structural depth correlation is clearly continued to the south-east of Tarbert in the second cross-section.

Fig. 3.30 shows a simplified lithological map and cross-section. Garnet zone rocks are semipelitic while biotite zone rocks are dominantly mafic and carbonate-rich at lower grades, and phyllic at higher grades. Thus, metamorphic
Fig. 3.29 (a) Schematic cross-section through the Loch Awe Syncline and the Tay Nappe with the positions of the Knapdale garnet isograd of Graham et al. 1983, and the southern limit to the garnet zone as set at Tarbert by Tilley (1925); metamorphic grade increases to Tarbert; if lower grade rocks are present immediately to the south-east of Tarbert, steep temperature gradients during metamorphism are implied. The temperature gradients may need to be inverted since the rocks to the south-east are from deeper structural levels.

(b) The same cross-section as in Fig. 3.29(a), but with a tentative south-eastern garnet isograd set in Northern Kintyre, based on the presence of garnet relics in sample 87-8. The line is poorly constrained due to the absence of Barrovian assemblages in Northern Kintyre.
Fig. 3.30 Simplified lithological map and cross-section of Tayvallich, Knapdale and Northern Kintyre: the biotite zone has a high proportion of mafic and carbonate-rich rock, while the garnet zone in Knapdale has a higher proportion of semi-pelitic rock. Thus, the grade of primary metamorphism is correlated in Knapdale with structural depth and lithology. These correlations break down to the south of Tarbert if Tilley's garnet isograd is accepted.
grade is not only correlated with structural depth in Knapdale and Tayvallich, but also with the lithology present on the surface. At present, the link between metamorphic grade and lithology may seem tenuous, but one of the recurring themes of this thesis will be the suggestion that variations in crustal composition have influenced metamorphic grade by associated variation in radiogenic heat production. This suggestion is addressed in full in chapter 7, but briefly, mafic rocks are expected to have lower abundances of heat producing elements, so crust rich in mafic rocks can be expected to reach lower temperatures than crust poor in mafic rock.

As with the grade-structural depth correlation, the grade-lithology correlation breaks down if the southern limit of the garnet zone is set at Tarbert, since crust dominated by semi-pelitic rocks and absent in mafic lithologies makes up the exposed rock in Northern Kintyre. Thus, the position of the southern limit to the garnet zone advocated here is more consistent with what would be expected to be the major controlling factors of regional metamorphism, namely structural depth and lithological type. Also, the presence of almandine-grossular garnet in Northern Kintyre proves that the garnet zone extends further south than hitherto thought.

The question of the syn-D1 geometry of the Tay Nappe can be answered by study of the metamorphism in the South-West which occurred during D1, and the basic correlations of lithology and structural level with metamorphic grade just discussed. Harte and Dempster (1987) discussed the narrowing of isograd spacing seen at the far Eastern Highland Border near Stonehaven explaining it in terms of horizontal heat flow as a result of juxtaposition of cool rock against warmer rock along a precursor lineament to the Highland Boundary Fault. Comparable narrowing of isograds is unlikely in the South West Highlands; even with the isograd distribution argued for above, the Highland Border is 20 km to the south east of garnet zone rocks so horizontal temperature gradients will not be large. It is clear that rock to the south east have been lowered structurally relative to rock in the north west since D1-D2 deformation and the primary metamorphism, resulting in rotation of the south eastern garnet isograd surface to the south east. The rocks now forming the Knapdale Steep Belt must therefore have had a North-Westerly dip, but this would have been shallower than now as described in chapter 2. Thus the Tay Nappe would have formed as an inclined tight to isoclinal fold (Fig. 3.31) whose closure would have been rotated to the south east by
Fig. 3.31 Suggested geometry of the Tay Nappe immediately after primary deformation and metamorphism with the suggested primary metamorphic isograds superimposed: The isograds define a thermal anticline-syncline pair (cf. Kennedy 1948, Chinner 1985), the syncline centred on Tayvallich.

Fig. 3.32 Possible thermal structure for the Dalradian crust of the South West Highlands immediately before $D_1$-$D_2$ folding, based on the suggested post-$D_1$-$D_2$ isograd structure in Fig. 3.31: again, the isotherms define a thermal anticline-syncline pair.
subsequent deformation.

3.5.3 Isotherms and Folding:

The simultaneous metamorphism and major reclined to isoclinal folding discussed above, implies that the syn-metamorphic thermal structure of the crust may have been disturbed at this time, though the regional isograd geometry is not well constrained at present, especially in the south east of Tarbert. Thermal anomalies (folded or overturned isotherms) may well have formed and may be preserved in the regional metamorphic isograd geometry. The possibilities for such preservation are addressed here.

Thermal anomalies are generally short length-scale features with steep temperature gradients associated with them. It is known that time-scales of heat transfer by conduction are proportional to the square of length-scales and that heat transfer rates are proportional to temperature gradients (section 7.2). Therefore, thermal anomalies of the kind considered here are transient features. Their formation will be favoured by rapid strain (Shi and Wang 1987) or major contrasts in thermal properties (Pinet and Jaupart 1987), and their preservation as regional metamorphic isograds will be favoured by rapid cooling (Crowley 1988).

Based on what has been suggested concerning the geometry of isograds in the South West Highlands, immediately prior to D₁ deformation, the crust might have had a thermal structure similar to that in Fig. 3.32 The isotherms in the South-East would have been elevated in crust dominated by semi-pelitic rocks, and depressed in the North West in crust dominated by mafics and carbonates. Then, as described in chapter 2, the inclined tight to isoclinal proto-Tay Nappe and Islay Anticline would propagate out from their root in the Loch Awe Syncline as a result of North West-South East compression, the fold hinges rolling clockwise (Tay Nappe) or anticlockwise (Islay Anticline).

If strain rates were high during this folding, heat may have been advected and isotherms deflected resulting in the production of thermal anomalies, which would last as long as the duration of folding (Fig. 3.33). If, however, the strain rates were low, little significant deflection of isotherms will take place. Any thermal anomaly produced by the advection of heat during the folding will then re-equilibrate by thermal relaxation relatively quickly. If regional cooling rates are high at this
During Folding

Immediately after Folding

Mafic rock-rich crust

Propagating Tay Nappe

Initially inclined Tay Nappe

500 deg. C isotherm:

--- High strain rates

----- Low strain rates

Fig. 3.33 Two alternatives for the extent of deflection of isotherms during Tay Nappe emplacement: rapid strain rates lead to large deflection, and possible over-turning of isotherms, while slow strain rates lead to little deflection of the isotherms.
stage, any isograd structure caused by the thermal anomaly will be preserved and its geometry will be similar to that of the thermal anomaly. If, however the rocks cooled slowly, any isograd structure formed will be swamped by the reequilibrating isotherms, the cool rocks at deep levels rapidly reaching similar temperatures to those in the core of the anomaly.

Very high horizontal strain rates lead to overturning of isotherms resulting in inverted isograds. It has already been suggested that if the southern limit of the garnet zone was set at Tarbert, the resultant isograd may be inverted, because deeper structural level rocks are present to the south-east of this line. It is also possible that the south-eastern garnet isograd inferred in Fig. 3.29 could be inverted, again because rocks at a deep structural level are present to the south-east of it. Watkins (1984, 1985, 1987) and Chinner (1985) have argued forcefully for the presence of inverted metamorphic zones along the entire south-eastern margin of the Scottish orthotectonic Caledonides. At present, not enough is known about the geometry of the south-eastern garnet isograd, wherever it is positioned, to decide whether it is inverted or not, but clearly, if it is, this inversion has major implications for both strain rates during emplacement of the Tay Nappe and cooling rates after the primary metamorphism; if the isograd is inverted, it requires that temperatures at the primary metamorphism were the highest attained in the crust volumes concerned, and that strain rates during emplacement of the Tay Nappe were high. The next section is devoted to the specific question of the existence of inverted metamorphic zones in the Dalradian and is based on a critical review of other studies, from the perspectives developed in this thesis.

3.6 The South-Eastern Garnet Isograd: Is It Inverted?

Watkins (1984, 1985, 1987) has presented detailed evidence for the garnet isograd in the West Central Highlands at Balquidder being inverted, and Chinner (1985) speculated that the other, higher grade, Barrovian zones along the entire South-Eastern margin of the Scottish Caledonides may have suffered a similar fate. The studies of Watkins used the presence of over 1000 metres of vertical relief to map a line separating garnet-bearing rocks from garnet absent assemblages and to demonstrate that the garnet-bearing lithologies occupy topographically and structurally higher positions, concluding that higher grade
rocks lie on top of lower grade rocks.

There are many apparent similarities between the metamorphic histories of Balquidder and the South-West Highlands although Watkins has tended to equate the prograde metamorphism in Balquidder to a Central Highlands (syn-D₃) scheme rather than a South-West-Highlands-like pattern; these similarities will be discussed further below. The occurrence of primary metamorphism during D₁-D₂ deformation in the South-West has already been demonstrated, and the Balquidder area will be looked at from this perspective. This is not based on personal study, but on the descriptions of Watkins. Firstly, however, suggested mechanisms for the production of a negative temperature-depth gradient will be reviewed, then the specific problem of the Dalradian inversion will be addressed.

3.6.1 Inverted Isograds; How They Form:

Inverted isograds form either by the presence of a negative temperature-depth gradient during metamorphism, or a previously-formed normal isograd sequence can be reversed or overturned by subsequent tectonic activity. Perhaps the best known inverted isograd sequence is that preserved in the Himalaya. The presence of up to 5000 metres of vertical relief makes the existence of the inverted metamorphic sequence unequivocal. Le Fort (1975) suggested a model invoking the thrusting of hot rock over cold, the resulting localised negative geothermal gradient being preserved as regional metamorphic mineralogy. The resultant thermal profile immediately after instantaneous thrusting is equivalent to saw-tooth geotherms which define the starting conditions in the thermal models of England and Richardson (1977). A saw-tooth geotherm is essentially a short length-scale thermal anomaly with very steep temperature gradients across it. It therefore decays into a smooth, depressed geotherm within a very short time of thrusting, and rapid uplift and cooling rates will be needed to preserve the reversed geothermal gradient as an inverted isograd sequence.

Like most inverted isograd sequences, the Himalayan sequence is associated with major thrusting. Two models which produce negative geothermal gradients by shear heating during thrusting are those of Graham and England (1976) and Brewer (1979). By accounting for rheological weakening of rock during dehydration reactions, the Graham and England (1976) model gives temperatures no higher than 500 deg.C at geologically realistic strain rates, while the Brewer
(1979) model gives higher temperatures as it assumes that the mechanical properties of the rocks are not temperature-dependent. Thus the major mechanical problem with the production of inverted temperature-depth profiles is that very high strain rates are needed to perpetuate the anomaly, and to prevent its rapid decay. While a negative temperature-depth profiles in the crust are possible conceptually, there are major problems with their preservation as metamorphic sequences.

3.6.2 The Dalradian Case:

In the Dalradian example, there are two major differences between it and most other inverted isograd sequences. These are:

1. the absence of associated major thrusting,
2. the absence of compression of the isograd sequence:

This inverted sequence is therefore apparently as a result of a large length scale, normal temperature gradient thermal anomaly with no immediately obvious means of generating, or perpetuating it.

It was indicated above that the metamorphic histories of the South West Highlands and Balquidder share many similarities. Some of the similarities involve the secondary, overprinting assemblages to be described in detail in chapter 4, and whose equivalents in Balquidder were studied by Watkins (1983). The similarities are:

1. Protoliths from both areas are from the Southern Highland group - the Beinn Bheula Schists in the South West and the Pitlochry Schist in Balquidder - and are both on the inverted limb of the Tay Nappe. They both, therefore occupy the same structural position and are stratigraphically directly along strike of one another. This is not strictly a similarity in metamorphism, but an indication that controlling factors of regional metamorphism (bulk rock composition, heat production rates etc...) in both areas are likely to be similar.
2. Both areas bear widespread secondary metamorphic assemblages. The Albite Porphyroblast Schists (section 4.2, and Watkins 1983) are the first stages in the secondary metamorphism in both areas, although they are not described to the North-East of the Bridge of Balgie Fault which divides the Balquidder area in two (Fig. 2 of Watkins 1983)
3. Muscovite-chlorite bearing, biotite absent assemblages are present in both areas. In the South West Highlands, these assemblages are almost always
associated with secondary metamorphic fabrics, textures and mineralogy, often bearing albite porphyroblasts. No such observation is made in Watkins' studies.

4. P-T conditions of prograde metamorphism are very similar in both areas (chapter 5, Watkins 1985). The stress here is on the medium to high pressures (>9 Kbar) and low to medium temperatures.

The major difference between the South West Highlands as described here and Balquidder as described by Watkins lies in the timings of the various metamorphic events relative to the deformational histories. The garnet isograd drawn by Watkins cuts a previously unrecognised D2 fold, the Ben More Synform, which is suggested as de-inverting much of the Loch Tay Inversion. (Watkins 1984). This relationship is used to infer a Central Highlands-like post-D2 to syn-D3 timing for primary metamorphism rather than during major inclined to recumbent folding -D1. The result of this inferred timing of metamorphism at Balquidder is that no means of overturning the isograd by folding can be invoked.

The status of the proposition that metamorphism occurred under a negative geothermal gradient therefore rests on two factors:

1. The timing of metamorphism relative to deformation: this timing, according to Watkins, requires that metamorphism occurs during a tectonically quiet period after recumbent folding and inversion of bedding had ceased. This in turn rests on the status of the Ben More Synform.

2. The status of the mineralogical and petrological changes occurring across the isograd as prograde metamorphic features: the presence of widespread retrogression to the south-east of the highest grades developed in both areas raises the possibility that the line mapped as an isograd is in part a front of secondary metamorphism.

The main pieces of evidence put forward by Watkins (1984) for the timing of metamorphism relative to deformation are that the albite porphyroblast schists are concentrated along D4 monofoms and that his garnet isograd cuts a fold assigned to D2. These are used to infer growth of albite porphyroblasts during D4 deformation, which "allows" the primary metamorphism to occur during D3 deformation. Evidence will be presented in chapter 4, however, linking the albite porphyroblasts to the D3 phase of deformation. This is based on the styles of micro-folding preserved as inclusion trails close in style to folds assigned in outcrop in other parts of the Dalradian to D3 (shearing and rotation of S1) and the rarity of D4 penetrative cleavages.
Because virtually identical mineralogies and textures are preserved in both areas, it seems reasonable to infer that the secondary assemblages grew during D₃, rather than during D₄. In addition, the similarity between the earlier assemblages in the South West Highlands and Balquidder makes it reasonable to infer that both sets of primary assemblages grew at about the same time, that is during the primary, D₁-D₂ deformation. Thus, if Watkins’ isograd is a primary metamorphic feature, it cannot cut a D₂ fold, and if the line drawn as an isograd cuts a D₂ fold, it cannot be a primary metamorphic isograd.

In Watkins (1987), little attempt is made to relate apparently progressive metamorphism to fabrics and textures except to state the ambiguity that garnets have straight inclusion trails (cf. Bell *et al.* 1985, Vernon 1988, in press, see also section 4.1). Most of the evidence presented is in the form of triangular diagrams of continuous changes in mineral chemistry. As these are continuous (sweeping tie lines, not crossing), and concern fabric forming minerals (ie micas and chlorite) they cannot on their own distinguish the direction in which the reactions concerned have proceeded. This (or these?) direction(s) might be progressive, or it (they?) might be retrogressive (or both).

The data associated with increasing grade across the garnet isograd as drawn by Watkins are also ambiguous when it is realised that a retrogression may have left the originally highest grades unaffected, just affecting the lower grades of what may have been a normal isograd sequence.

Finally, the assemblages at Balquidder, their order of development and their spatial relationships to the structure of the area are very similar to those in the South West Highlands. It has already been suggested that metamorphic grades in the South West Highlands increased from Tarbert south-eastward into regions pervasively overprinted by secondary metamorphism. It will be demonstrated in chapter 4 that the rocks in Northern Kintyre are unlikely to stabilise Barrovian assemblages due to their oxidised nature. The same rocks are present structurally below Watkins’ inferred isograd, and are also affected by pervasive secondary deformation and metamorphism (Watkins 1983). It is therefore very difficult to draw Barrovian isograds in Northern Kintyre (which is why the garnet isograd drawn in Fig. 3.29 is approximate); the inferred position of the isograd in Balquidder must therefore be suspect, and probably does not reflect the thermal structure of the crust during metamorphism at Balquidder.
To summarise, the ambiguities and objections to the presence of an inverted garnet isograd along the south-east of the Scottish Caledonides are as follows:

1. the data relating the timing of metamorphism and deformation are insufficient to confirm the trends inferred by Watkins. Based on the information available from the South West Highlands prograde metamorphism probably took place much earlier, relative to the deformational history, than inferred by Watkins.

2. The petrological data are unable to distinguish between progressive and possible retrogressive trends. If there was significant retrogression unrecognised by the data presented, the isograd position as mapped may depend to a large extent on this.

3. Any isograd separating Barrovian assemblages drawn in such rock as is present in Northern Kintyre and Balquidder will be very suspect, because of the probable alteration of the usual sequence of mineral assemblages by the $f-O_2$ conditions of metamorphism.

I cannot refute unequivocally the proposition that metamorphism took place under a negative temperature-depth gradient, but I hope to have demonstrated that the proposition has not been demonstrated convincingly either. This is due to potential, unrecognised complexities in the post-primary metamorphic history and bulk rock compositions that have been seen in the very similar rocks in the South West Highlands. While little petrographic data is presented for Balquidder, the petrography of the primary assemblages in the South West indicates an early, syn-D$_1$ primary metamorphism. This is supported by geochronological data (chapter 6, cf. Dempster 1985). Thus while the Balquidder metamorphism has been related in time to the Central Highlands metamorphism using suspect or sparse structural and petrographic data, I feel that the information available to me (good petrographic and geochronological constraints) shows that this relation must be wrong and that the metamorphism in Balquidder follows a "South-West Highlands" pattern rather than a "Central Highlands" pattern.

It is also clear that pervasive, regional scale secondary, overprinting metamorphism has affected both the South West Highlands and Balquidder. A syn-D$_1$ thermal structure like that shown in Fig. 3.33 re-imposes "the tyranny of the thermal anticline" (Chinner 1985) in the South West Highlands and at Balquidder.
The models of Crowley (1986) indicate that thermal anomalies are only preserved as isograds if the rates of cooling in the regional-scale metamorphic belt were fast, as measured by rates of uplift. Therefore, the ultimate test of whether inverted isograd sequences can have formed in the Dalradian, is to find the regional rates of cooling from the peak metamorphic temperatures. This is done in chapter 6 using geochronological data.

3.7 Conclusions of this Chapter:

The main conclusion of this chapter is that the primary metamorphism occurred during the earliest-preserved regional deformational episode. Thermal models of regional metamorphism (England and Richardson 1977, this thesis chapter 7) show that 10-100 Ma time-scales are necessary for heating and cooling as a result of crustal thickening. Thus, the Tay Nappe formed at deep and hot enough levels in the crust for garnet to grow, and the thickening event that was probably necessary to produce Dalradian regional metamorphism occurred independently of the formation of the Tay Nappe; the Tay Nappe does not constitute the primary thickening event of the Caledonian Orogeny. As a result, both the Tay Nappe formation and the primary metamorphism may have the same cause, and may be inter-related by feedback loops involving attainment of high temperatures, the presence of deformation, and of fluid infiltration which may well be present in most other regional metamorphic terrains.

Other conclusions drawn in this chapter are as follows:

1. The pelitic assemblages developed during the primary metamorphism depend on bulk rock Fe/Mg and Si/Al ratios. The "usual" trend of high Fe/Mg ratios favouring the growth of higher grade mineralogy at a given temperature are apparent, but high Si/Al ratios also favour the growth of higher grade mineralogy at given conditions. Thus, when assessing the factors governing the growth of differing pelitic assemblages, both Fe/Mg and Si/Al ratios need to be considered.

2. This metamorphism was accompanied by at least two fluid infiltration events in the lower grade rocks; the first causing hydration of originally dry rocks, and the second causing overprinting of the earlier hydrous assemblages by carbonaceous mineralogy. The second fluid was derived by regional dehydration of higher grade rocks at lower levels.

3. The highest grade Barrovian assemblages in Knapdale and Tayvallich were developed in those areas which are at the deepest structural levels and are dominated by the most pelitic, least mafic lithologies. Similar correlations can be drawn with the degree and styles of regional deformation with the
weakest rocks undergoing the most strain. The weakest rocks are predicted by mechanical models to be the most quartz and phyllosilicate-rich and the warmest. Both these influences reinforced one another in the South West Highlands.

4. The close links between regional scale folding and nappe emplacement, and the probable attainment of the highest temperatures imply that heat may have been advected to the extent that regional isograds may have been deflected, or possibly inverted. It cannot be decided which of the two possible alternatives are correct at present, but the re-location of the garnet isograd making the fit with lithologies and structural levels better than before, and the ambiguity and lack of constraint offered by studies in other areas tends to favour the absence of inverted metamorphic zonation.

5. Simple thermal constraints and the close link between nappe emplacement and the development of isograds means that the early attitudes of the large scale primary folds can be elucidated. The Tay Nappe was originally inclined to recumbent; its shape was subsequently modified by secondary deformation, accompanied by secondary overprinting metamorphism.

The next chapter examines the secondary tectonic and metamorphic episodes more closely.
"Stonehenge is incomprehensible until we realise the builders needed some kind of scaffolding, or ramps of earth WHICH ARE NO LONGER THERE. We can only see the end product, and have to infer the vanished scaffolding..."

Richard Dawkins, The Blind Watchmaker

In the construction of P-T-t histories of regional metamorphic terrains, metamorphic episodes involving the overprinting of the dominant primary assemblages, normally inferred to have grown at (P-T)\textsubscript{S\text{max}} provide valuable constraints on post (P-T)\textsubscript{S\text{max}} histories. If, in addition, a specific deformational episode can be linked to the retrograde metamorphism, useful time markers will result, especially if fabric forming minerals are produced. These minerals can be dated, providing absolute time constraints on the post (P-T)\textsubscript{S\text{max}} history. In addition, if the P-T conditions of the secondary metamorphism can be characterised, or at least inferred, the shape of the post-(P-T)\textsubscript{S\text{max}} portion of the P-T-t path can be constrained, along with the cooling and uplift rates from the differences in pressure, temperature and time between the primary and secondary assemblages. It is for this reason that secondary overprinting metamorphism developed in parts of the study area has been studied in detail. Firstly, the microstructural and textural patterns in these rocks will be described, leading to derivation of the style and influence of deformation. Then, mineral assemblages, reactions and phase equilibria will be described, so that P-T conditions can be derived in subsequent chapters.

This chapter will fulfill a similar role to chapters 2 and 3 for the secondary metamorphism, constraining the later stages in the area's P-T-t histories by description of the fabrics, textures, mineralogy and phase equilibria of later mineral assemblages overprinting the primary, prograde regional mineralogy.

The later overprinting assemblages are developed in Northern Kintyre and Southern Knapdale, and are therefore confined to the deeper structural levels where secondary deformation is most intense (chapter 2). The relatively localised development of the later mineralogy has resulted in the south-eastern garnet
isograd being obscured so that its presence in Northern Kintyre had not been recognised previously. Instead, prior to this study, the south-eastern garnet isograd had been drawn near to the edge of the zone affected by secondary metamorphism (see chapter 3). Metamorphic episodes producing locally developed overprinting assemblages are usually, but not always, retrograde in nature, in that the overprinting assemblages are more hydrous and are stable at lower temperatures than the assemblages being overprinted. However, it will be shown that the earliest stages in the secondary metamorphism in the South West Highlands occurred while the rocks were at temperatures close to those of the primary metamorphism. For this reason, the term "retrograde" is avoided in this chapter.

The chapter is in two parts, reflecting the treatment of the primary deformation and metamorphism in chapters 2 and 3. The first part deals with the textures and fabrics associated with secondary metamorphism, and relating these to the regional deformational history, while the second part discusses the mineral assemblages, chemistry, and phase equilibria developed during the secondary metamorphism.

4.1 Microstructures and Microtextures of Secondary Assemblages; Principles:

This section is aimed at setting the ground rules to be used in interpretation of the textures and microfabrics developed in secondary assemblages. The most detailed study has been carried out on the inclusion trails preserved in overprinting albite porphyroblasts, specifically on the geometries of these trails in relation to fabrics seen in the matrices of these rocks. The question to be answered in this, and the following section is how the inclusion trails form and how they relate to the larger scale deformational history of the region: that is, in which deformational event did growth of these porphyroblasts and assemblages take place? The result will be a qualitative study of the behaviour and physical properties of a rock as it undergoes deformation and growth of a porphyroblast phase.

It will become clear that the interpretation placed on a specific inclusion trail geometry depends to a very large extent on the model used for the interpretation. As a result, caution needs to be exercised otherwise, ambiguities in interpretation
can be rationalised to fit personal bias, rather than scientific criteria that are derived objectively. Whenever a set of diagnostic criteria are derived for a specific type of problem, their use in an unquestioned way assumes the absolute consistency of their derivation, and ambiguity may not be recognised. Therefore, any such set of diagnostic criteria should be applied carefully, and only if their means of derivation are satisfactory. It is easy to produce a set of criteria based on closed argument - assuming the truth or consistency of an argument, then using this assumption to interpret an observation as purportedly proving the truth of the argument. Ideally, the derivation of the set of criteria should only depend on observation and should not depend on assumption. This section will therefore review the models normally used for microtextural work and arrive at a decision as to how textures will be interpreted.

Essentially, models for porphyroblast textures fall into two groups; those models which allow porphyroblasts to rotate relative to their matrix, and those models which prohibit rotation except under exceptional circumstances. The first group of models is based on the criteria of Zwart (1962) which have been enormously influential, especially as they were re-iterated by Spry (1969). The second group of models has been derived more recently and sets out to reconcile ambiguities in the first group. One such model has been advocated most forcefully by Bell and co-workers, as an answer to the problems associated with the Zwart criteria discussed by Vernon (1978). The models of Zwart and Bell et al. will be reviewed in turn.

4.1.1 Rotating Porphyroblasts; The Zwart Criteria:

Zwart (1962) attempted to answer the problem of timing the growth of minerals making up a progressive metamorphic sequence, using constrained deformational events as time markers. The problem was that while the phases in an aligned schistosity could be said with confidence to have grown simultaneously, the same could not be said about porphyroblast phases (which by their nature tend to be used as zonal index minerals) even when these were in apparent textural equilibrium with the matrix phases. Zwart distinguished three types of deformation: shearing, flattening, and microfolding. According to this model, these produce specific fabric geometries which are preserved as inclusion trails in porphyroblasts. The shapes of the inclusion trails depend on whether the grain grew before, during or after the deformation producing the matrix fabric. Thus
nine types of geometrical relationship are distinguished (Fig. 4.1).

It must be stressed that when using the Zwart criteria, growth of a porphyroblast is timed relative to the last conspicuous deformation preserved in the matrix. A porphyroblast phase can be syn-kinematic with respect to an earlier fabric and pre-kinematic to an overprinting crenulation. This method can therefore set out to time growth of different porphyroblast phases in a polydeformed metamorphic belt whose deformational history is already well known.

There are, however, at least two major problems associated with the Zwart criteria. The first involves the manner in which the criteria were derived. This was very strongly dependent on assumptions. Some of these assumptions involved the suggestion that geometrically congruent fabrics grew at the same time throughout the metamorphic belt, as well as the idea that growth of a fabric occurs very rapidly in comparison with the timescales of regional metamorphism. As a result, a specific geometry of folds and fabrics records an instantaneous event which is said to occur simultaneously throughout a metamorphic belt. These two assumptions or hypotheses were not testable when the Zwart criteria were derived and are unlikely to remain inviolate. The Zwart criteria do, however, take these assumptions for granted and depend on them for their consistency. In addition, as reviewed by Vernon (1978), interpretations using the Zwart criteria were subject to a large degree of ambiguity unless used with great care and unless the constraints are good. Potential ambiguities with each of the possible interpretations from the Zwart criteria are too numerous to be listed here but are due generally to one or more of three reasons:

1. whether porphyroblast growth is considered relative to the GROWTH of the fabric, or relative to a later deformation of this fabric;
2. lack of knowledge of the mechanical effects of the growth of porphyroblasts on an actively deforming matrix;
3. whether a porphyroblast grows by pushing the matrix out of the way, or by volume for volume replacement.

These potential ambiguities are discussed below.
Fig. 4.1 The geometrical relationships of porphyroblast inclusion trails with the matrix orientation as inferred by Zwart (1964): three styles of deformation are recognised, and porphyroblast growth can occur either before, during, or after deformation (from Zwart 1964).

Fig. 4.2 Generalised strain field resulting from partitioned deformation: zones dominated by shearing strain envelope zones dominated by shortening strain, which surround in turn strain-free zones (from Bell 1986).
4.1.2 Non-rotating Porphyroblasts; Deformation Partitioning:

Based on the realisation that rocks are heterogeneous and therefore respond variably to a given stress, Bell and co-workers (Bell 1985, 1986, Bell and Rubenbach 1983, Bell et al. 1986) described the growth of porphyroblasts and the evolution of microstructures with a deformation partitioning model. In this model, porphyroblast growth invariably occurs in the presence of deformation, and a rock volume undergoing deformation behaves in one or more of four different ways:

1. they take up no strain
2. they take up progressive co-axial shortening strain only (no shear component)
3. they take both shortening and shearing strain
4. they take up shearing strain only.

Hence, deformation occurs either with, or without, a shearing component.

Evidence for variable response to stress was to be found in the presence of planar fabrics of aligned low-shear-strength phases (e.g., sheet silicates), lying between zones of unaligned, higher-shear-strength mineralogy. In other words, the presence of schistosity in metamorphic rocks means that shearing deformation is concentrated. All of these observations were used to produce a model for the growth of porphyroblasts in a deforming rock. In contrast to the Zwart criteria, this model was conceived as a result of observation; its consistency is not dependent on assumptions which may be untestable.

If a rock is stressed, the style and rate of strain will depend on mineralogy, but a generalised resulting strain field is shown in Fig. 4.2. Here, strain-free domains are surrounded by zones of shortening strain only, surrounded in turn by zones of shortening and shearing strain, which in their turn are enveloped by bands of shearing strain. In the case of a real rock, the bands of shearing strain correspond to planes of schistosity while the zones of shortening strain are dominated by phases with a higher shear strength.

In this model, complex inclusion trail patterns in porphyroblasts form as a result of overgrowth of de-activated micro-shear zones. During deformation, rocks will undergo different styles of deformation at different times. If the growing edge
Fig. 4.3 Edge dissolution of a growing porphyroblast impinging on an active shear strain zone: This diagram suggests that porphyroblasts on which a couple is exerted will not rotate but will be dissolved at their edges instead.
of a porphyroblast impinges onto an active micro-shear zone, it is likely to be dissolved, so the micro-shear zone is not crossed when active, but only when de-activated. As a result, the geometry of the shear zone is preserved as an inclusion trail. The major implication of this model is that inclusion trail geometries can be used to analyse the style of the deformation that was occurring during the growth of the porphyroblast. Hence, as with Stonehenge, the scaffolding is inferred. It must be stressed that shearing may be still occurring in another part of the rock while a de-activated shear band is being overgrown. The geometries of inclusion trails will therefore vary between grains of a porphyroblast phase, even if they grew simultaneously.

Thus the difference between the assumptions behind the Zwart criteria and the premises on which the model of Bell et al. is set is that consequences of the latter can be predicted and compared with observation while the former are only assumed to have occurred. There are many implications to be drawn from this model, some of which are:

1. The lack of a shear component in areas in which porphyroblasts grow means that they will not rotate; the porphyroblast growth zone is locked in place as shearing deformation is partitioned around it.
2. Most, if not all, porphyroblasts will grow during active deformation; that is, they grow syn-kinematically.
3. Zones dominated by shortening strain form pressure shadows and/or augen during or after a phase of porphyroblast growth.
4. The lack of rotation of both porphyroblasts and pressure shadows means that previously existing fabric alignments are preserved as inclusion trails with the result that much information on the earlier stages of the rock’s deformational history can be derived providing a very valuable tool for structural, metamorphic, and tectonic analysis. This implication of the model is the most useful with respect to the aims of this thesis, because the style of the deformation can be analysed.

4.1.3 Discussion; Which Model Is Better?:

It should be clear from the foregoing that I consider the Bell et al. model to be superior to the Zwart criteria. The predictive and explanatory powers of the Bell model are greater as the model explains much that cannot be accounted for by the Zwart criteria, and, as a result, removes much that is ambiguous and contradictory. The logical foundation of the Bell et al. model is also much firmer than that of the Zwart criteria. Here, examples are given of the improvements of
the Bell et al. model over previous ideas.

The first major series of ambiguities in the Zwart criteria is concerned with timing relative to deformation. If a given phase has varying inclusion trail geometries between grains, according to the Zwart criteria more than one growth episode of this phase may have occurred. Grains with straight inclusion trails may be interpreted to have grown pre-tectonically, although they could have grown post-tectonically in a fabric produced by shear or compression. Grains with non-planar inclusion trails would have grown either post- or syn-tectonically. All these possibilities are shown on Fig. 4.4. On the other hand, the Bell et al. model can be used to interpret these porphyroblasts as all having grown simultaneously. Those with straight inclusion trails would have grown within a progressive shortening strain zone, while those grains with non-planar trails would have overgrown de-activated shear bands. These, on deactivation, continue to undergo shortening strain, allowing porphyroblasts to overgrow them (Fig 4.5).

The other major source of ambiguity in the Zwart criteria is that of not knowing whether a growing porphyroblast is physically capable of pushing fabrics aside as it grows. According to the Zwart criteria, a porphyroblast with a fabric draped around it could either have pushed the fabric aside by the "force of crystallisation", or the fabric may have been compressed in a direction more or less normal to its alignment after growth of the porphyroblast (Fig. 4.6). There has been much argument over the years as to the magnitude and ability of a force of crystallisation to deform a fabric (see Wheeler (1987)). The Bell et al. criteria circumvent this problem by implying that deformation partitions around the zone in which porphyroblast growth occurs. The presence of a porphyroblast is sufficient to divert shear strain bands around it, so the interpretation of this texture does not depend on the ability of the porphyroblast to push fabrics aside by force of crystallisation. The ability of the "force of crystallisation" to push fabrics aside is unconstrained. To make an unambiguous judgement in this situation requires this constraint, so a judgement made on this matter with the Zwart criteria must be suspect. Thus the Bell et al. criteria imply either that the porphyroblast existed prior to modification of the fabric, or that flattening occurred during growth of the porphyroblast. The ambiguity here would be removed by inspection of inclusion trails for continuity with the matrix fabric (Fig. 4.7).

To summarise, the major differences between the Bell et al. criteria and the
Fig. 4.4 Possible ambiguities in interpretations based on the Zwart criteria: a given phase has more than one type of inclusion trail geometry.

Fig. 4.5 The same geometrical relationship as in Fig. 4.4, but interpreted by the deformation partitioning model with less ambiguity:
Possible ambiguities in interpretation based on the Zwart criteria: did the grain push the surrounding rock aside as it grew, or was the rock compressed normal to the schistosity after the prophyroblast had grown?

Fig. 4.7 The same geometrical relationship as in Fig. 4.6, but interpreted by the deformation partitioning model with less ambiguity: the interpretation can vary, but requires detailed study of the inclusion trail-matrix relationships.
Zwart criteria are that the former only allows porphyroblasts to grow during a deformational episode, and does not normally allow them to rotate either during or after their growth. This allows interpretation of a set of porphyroblasts with contrasting inclusion trail geometries as having grown during a single deformation, preserving the alignment of deactivated shear bands by overgrowth of these by the porphyroblast. On the other hand, the Zwart criteria allows rotation as well as growth during a tectonically quiescent period.

The Bell et al. criteria also allow the elucidation of the tectonic style and geometry of deformation occurring during growth of a porphyroblast phase while the Zwart criteria cannot do this since to match an inclusion trail geometry to a specific deformational episode requires foreknowledge of the geometry of that episode. The Bell et al. criteria suggest that all porphyroblast growth occurs during deformation; their validity rest therefore on whether deformation is partitioned and whether porphyroblast growth can occur only during deformation.

Because rocks are heterogeneous, deformation partitioning will almost certainly occur, as confirmed by the ubiquitous presence of tectonic fabrics in deformed rocks. However, it does not necessarily follow that porphyroblast growth always occurs during deformation. Vernon (1988) makes the point that interpretation of a pattern as being due to post-kinematic growth depends on scale. A complex inclusion trail in a porphyroblast is evidence either of overgrowth of an evolving fabric or evidence of overgrowth of a fabric which is no longer active. In the latter case, deformation may still be taking place, but with high strain areas separated by scales larger than that of the porphyroblast, or the thin section. On very local scales, the cores of porphyroblasts record growth in the absence of deformation, because fabric alignments are often preserved as straight inclusion trails. Despite this, deformation is clearly present on larger scales, as recorded by curled inclusion trails at the edges of porphyroblast grains ("millipede" geometry).

The danger here is that syn-deformational growth may be adopted as an article of faith, meaning that its apparent absence on a thin section to hand specimen scale can be rationalised by invoking separation of high strain zones by greater length scales than those represented by the size of the area under observation. If a thin section has evidence for porphyroblast growth in the absence of deformation, deformation should be looked for. The best evidence for deformation-absent porphyroblast growth is in contact aureole rocks. However, intrusions can, and
do, deform country rocks, so it can be argued that deformation was present. What appears to be missing is proof that deformation is needed for porphyroblasts to grow; a study is needed which shows that deformation, or at least strain, is necessary for growth of porphyroblasts to occur.

Wheeler (1987) showed that very localised, and very large, stress concentrations are needed to drive diffusion along grain boundaries between two different phases, between which a new phase is growing. Transport of solutes along such a grain boundary is necessary, otherwise, the product phase of any reaction cannot grow. Potential driving mechanisms are discussed; only local stress concentrations within grain boundaries are sufficiently large to drive transport along grain boundaries. By realising that stress and chemical potential are related, potential gradients are set up by stress concentrations acting over smaller than grain size length scales. This study therefore indicates that strain is necessary for porphyroblast growth to occur.

The presence of undeformed fabrics in porphyroblast cores is interpreted by the Bell et al. (1986) model as implying the absence of deformation in the rock volumes concerned. This is apparently contradicted by the Wheeler (1987) model which requires that strain be present at the nucleation sites of porphyroblasts. This contradiction can be reconciled, however, by realising that the forces invoked by Wheeler (1987) act over far smaller length scales than those invoked by the Bell et al. model, and their effects will not be visible in the inclusion trail geometry.

4.2 The Petrography of the Secondary Assemblages:

Having reviewed some of the models for textures in porphyroblastic metamorphic rocks and decided upon the framework for interpretation of textures in this thesis, the data to be interpreted will now be presented. Then in following sections, the petrographic observations presented here will be interpreted according to the models of Bell and co workers.

The secondary assemblages are albite porphyroblast schists, previously studied in detail by Watkins (1983) and Evans (1961). These assemblages are developed over regional scales being recorded at Balquidder, West Central Highlands, and at Conemara (Yardley et al. 1987) as well as in Antrim and the South West.
Fig. 4.8 Map of the South West Highlands showing the extent of outcrop of albite porphyroblast schists: these make up the bulk of the secondary metamorphic assemblages in the South West Highlands (from Watkins 1983).
This section is dominantly petrographic, describing patterns, geometries, and relationships between mineral grains with a view to elucidating the deformational style and strain history during growth of secondary assemblages in the South West Highlands. Mineral assemblages, chemistry, phase equilibria and reactions will be discussed in more detail in sections 4.3 and 4.4. Texturally, a metamorphic rock can be divided very roughly into two parts; porphyroblast phases, and matrix.

Defining a porphyroblast as a sub-euhedral grain often, but not always, larger than other grains in the rock, and which does not conspicuously lie in a shear fabric, or schistosity, the following petrographic descriptions will treat porphyroblasts and matrix fabrics to a large extent separately.

4.2.1 Microfabrics:

In all the rocks studied in the South West Highlands which have been affected by secondary deformation, microfabrics are defined by geometrical and crystallographic alignment of sheet silicates and are of two types, microfolds, and penetrative cleavage cross-cutting the previous fabric. The degree of overprinting of the primary deformation varies from a mild crumpling to pervasive recrystallisation. As a result, a progressive or evolutionary history of secondary fabric formation can be traced from the changes in secondary fabric geometries with the degree of overprinting of the originally planar schistosity.

The pelitic assemblages unaffected by the secondary deformation are typical lower to middle epidote-amphibolite facies metasediments of the sort described in chapter 3 but include relatively high abundances of large, often twinned, ragged albite grains which may have been originally clastic, as the protoliths of these rocks were turbidite. These are wrapped by a mica schistosity, defining an augen texture. The first stages of secondary deformation and metamorphism are seen in assemblages such as these with very fine scale intergrowth of biotite and chlorite, recrystallisation of phengite, weak crumpling of the primary fabric, growth of a weak secondary fabric, and formation of small, inequant albite grains in the mica rich bands (Fig. 4.9).

The next stage of the textural development is seen in Fig. 4.10. In the rock shown here (87-07), abundant rounded, inequant porphyroblasts are aligned
Fig. 4.9 Initial stages in the development of the early secondary assemblages: primary fabrics undergo re-activation accompanied by growth of small albite porphyroblasts (specimen 87-11, cpl).
Fig. 4.10 Continuing development of the secondary assemblages: buckle-folding of the re-crystallised schistosity is accompanied by displacement of porphyroblasts so that they remain aligned parallel to the fabric (specimen 87-07, cpl)
parallel to the fabric at all times and are therefore displaced bodily with their surrounding matrix, during the folding. What has probably happened is that the earlier formed fabric has been buckle-folded only to the extent that shear in the fold limbs was absent; thus the deformation was not partitioned through the rock at this stage, but concentrated in the fold hinges in which there is evidence of dissolution.

Highly pervasive isoclinal microfolding and crenulation-cleavage formation are seen in specimen 87-12, shown in Fig. 4.17. In this rock, the mica-rich areas either have sub-parallel to parallel crenulations of a mica fabric or isoclinal folds with shearing along their limbs. Both these sets of structures lie between zones of low strain represented by a mica fabric aligned congruently throughout the rock. While the crenulation cleavages have the same sense of shear throughout the rock, the isoclinal fold limbs have opposite shear senses on each side of the fold. The axial planes of the isoclines are parallel to the crenulation cleavages. Despite this, the crenulations cannot really be called an axial planar fabric since they do not run into fold cores; each set of structures is developed in discrete zones of the rock. The formation of antithetic shear zones during the advanced stages of folding was described in detail by Bell (1986) and similar phenomena seem to be present here, especially in the limbs of the isoclines. This rock therefore represents the advanced stages of the folding whose earlier evolution is discussed above.

As secondary deformation and recrystallisation increases in intensity, the microfabrics become more complex (Fig. 4.12) with isoclinal folds, paired monoformal folds, box folds and shear bands all common. Assemblages in which the more complex textures are seen are all highly micaceous, and are therefore less competent than the more quartz rich rocks already described. The fabrics in the more complex patterned rocks often abut against the albite porphyroblasts and show other clear signs of recrystallisation after the growth of albite.

Thus, microfabrics in secondary assemblages record a history of progressive replacement of a planar primary fabric with a more homogeneously developed secondary fabric which is then folded and recrystallised in turn. The earlier folds are buckle-folds of the fabric with relatively little limb-parallel shearing. Later folds are tight to isoclinal folds of the same fabric with much more limb-parallel shearing. The latest folds preserved show the most complex patterns. Accompanying all the stages in secondary fabric development is the growth of
Fig 4.11 The alignment of inclusion trails in albite porphyroblasts is traceable between grains, even though the matrix fabric has been pervasively re-crystallised; these porphyroblasts have not rotated (specimen 84-22, cpl)
Fig. 4.12 Continued development of fabrics after growth of albite porphyroblasts: the fabric envelops the porphyroblast, and biotite is preserved in the resultant strain shadow (specimen 84-22, cpl)
porphyroblastic albite, possibly by the breakdown of elastic feldspar. In these assemblages, fabric development and microfolding generally outlasts the growth of porphyroblastic albite. The growth of the porphyroblasts in relation to the formation of fabrics will be considered next.

4.2.2 Porphyroblasts; Morphology and Inclusion Trail Geometry:

It has already been intimated that porphyroblastic albite is present in nearly all of the secondary metamorphic assemblages. These porphyroblasts, and their geometrical and textural relationships with their matrices are now to be described. There are two types of porphyroblast morphology; small, inequant grains with simple inclusion trail geometries, and larger equant grains with complex inclusion trails.

The first type of porphyroblast has a relatively simple textural relationship with the matrix. Inclusion trails of opaque grains, micas, epidote, and occasional garnet are always parallel to the alignment of fabrics in the matrix and rarely, if ever, show any crumpling. In most of the rocks in which these porphyroblasts are found, they occur in micaceous bands, sometimes with narrow zones of recrystallised phengite separating them from the quartz-rich zones surrounding them. It is clear that these porphyroblasts have not overgrown de-activated shear strain bands, as the inclusion trails are planar. However, it is probable that shear bands were present in these rocks during porphyroblast growth, presumably as the narrow, recrystallised phengite bands (Fig. 4.9). Hence, deformation was concentrated along the margins of these bands, with discrete shortening and shearing strain subzones present as the porphyroblasts grew within them.

The second type of porphyroblast is far more complex geometrically than the first type. Commonly, inclusion trails in the second type are planar in the cores of grains and curled to varying extents at the rims (Fig. 4.13). There are, however, many variations to this theme, as well as several exceptions. The straight portions of inclusion trails are often, but not always, parallel to one another in a given thin section, and usually continuous between grains in areas where many grains are closely packed (Fig. 4.11).

The curled trails at the edges of the porphyroblasts are either curled up at their edges, thus resembling the millipede geometry of Bell et al. (1986), or they
Fig. 4.13 Overgrowth of de-activated zones of shearing strain by an albite porphyroblast: the shear bands can only be overgrown if they are inactive, otherwise, the edge of the porphyroblast would be dissolved against them. The alignment of the de-activated shear zones is preserved in the inclusion trail geometry (specimen 84-22, cpi)
are sometimes folded (Fig. 4.14). Sometimes, bands of inclusion trails are wrapped around a central zone of planar inclusion trails. According to Bell et al. (1986), all these features represent varying extents of overgrowth of de-activated shear bands, active during earlier stages of porphyroblast growth (Figs 4.4 and 4.5). In other grains, microfolds are preserved as inclusion trails. Some grains appear to have overgrown zones of several de-activated shear bands separating zones of planar inclusion trails.

In many of the albite porphyroblast schists, primary metamorphic mineralogy is preserved as included grains, examples being sphene, epidote, micas, tourmaline and garnet. While the included garnets are often pristine, sphene in particular is often replaced by rutile and dolomite growing as pseudomorphs. The possible significance of this contrast is discussed more fully in sections 4.3 and 4.4, but the fact that the garnets are apparently stable during the growth of albite is the major reason why the secondary metamorphism is not referred to specifically as a retrograde event at this stage. In contrast, garnets are rimmed with chlorite in the matrix. Inclusion trails are rare in garnet porphyroblasts, but, where present, are straight or weakly folded. Again, straight inclusion trails in garnets in a given thin section are parallel to one another.

Fig. 4.15 shows inclusion trails in garnet porphyroblasts as well as in an albite porphyroblast engulfing one of the garnets. The inclusion trails in the garnet surrounded by the albite are parallel to the trails in the albite, but inclusion trails in other garnet porphyroblasts nearby are not parallel: the garnets have been rotated or displaced relative to one another and to the albite grain by subsequent deformation. Close inspection of the mica fabrics surrounding each of the garnets shows that as the fabrics are parallel to the inclusion trails in the garnets immediately adjacent, the rock has been divided into domains, each of which has been rotated relative to the other surrounding domains carrying the garnets with them.

The observation that inclusion trails in two different porphyroblast phases are parallel has two different explanations:

1. that both porphyroblast phases grew simultaneously relative to the deformational phases preserved in the rock:
2. The two phases grew during different deformational episodes, but that the inclusion trails reflect a preserved alignment that either predates both phases, or formed during the growth of the earlier-formed phase.
Fig. 4.14 More complex inclusion trail geometries in a single porphyroblast: microfolds and micro-shear zones are preserved (specimen 87-02CMG, cpl).
Fig. 4.15 Inclusion trails in garnets engulfed by albite: the trails in both phases are subparallel to one another, so they may have grown during the same deformational episode (specimen 71-2, cpl).
The first explanation is the kind that would be derived by use of the Zwart
criteria, although it could also be derived with the Bell et al. model, with the
straight inclusion trails in both phases reflecting zones of no strain and of
shortening strain only. That albite always overgrows garnet would be reconciled in
the first explanation by postulating that albite simply started growing later than
garnet. The second explanation would not normally be arrived at with the Zwart
criteria because these tend to equate congruent inclusion trail geometries in
various phases with the same deformational event. The observation just described
is not, as it stands, sufficient to decide which of the two explanations is correct.
More unequivocal information on the relative timing of deformation and growth
of both porphyroblast phases is needed. However, exclusive use of the Zwart
criteria in this situation would probably result in non-recognition of more than
one possible explanation of this texture.

An answer to the problem of the respective timing of albite and garnet growth
is provided in Fig. 4.16 which is also of a garnet grain partly engulfed by albite.
The inclusion trail in the core of the albite, instead of being planar, is draped
around the end of the garnet grain. In addition, there are signs of curling of
inclusion trails at the edge of the albite. The enveloping of the garnet would be
due to simple shearing during and after garnet growth according to the Bell et al.
model. This would produce a fabric and would be inactive during growth of the
albite; the geometry of this fabric being preserved by its being within the zone of
no strain now occupied by the centre of the albite porphyroblast. The alignment
of the curled trails at the edge of the albite grain is different to that of the
de-activated shear zone in the core, implying that syn-albite shearing was in a
different direction to syn-garnet shearing, and hence that growth of these two
phases was associated with two separate deformational episodes.

The main evidence for the growth of porphyroblasts during a deformational
episode, and the best information pertaining to the style of this deformation is
found in specimen 87-12 (Fig. 4.17), whose fabric has already been discussed. In
some zones of this rock, albite porphyroblasts are seen in low strain zones in
isoclinal fold cores and between crenulations, with inclusion trails continuous with
and congruent to the surrounding fabric. The ends of these grains sometimes
interdigitate into the fabric and are sometimes folded by a shear band. Other
porphyroblasts are rectangular, inequant, and aligned parallel to rotated and
recrystallised shear planes. Larger, equant porphyroblasts have complex inclusion
Fig. 4.16 Garnet engulfed by albite: the inclusion trails in the albite envelop the garnet, showing evidence for deformation after the garnet growth. The deformation must, however, have ceased prior to the growth of the albite; the garnet and albite therefore grew during two distinct deformational episodes (specimen CA 21, cpl).
Fig. 4.17 Evidence for the style of deformation in force during the growth of albite porphyroblasts: the deformation is dominated by tight to isoclinal microfolding and shearing, sometimes antithetic. Inclusion trails in albite porphyroblasts are usually congruent with the matrix alignment, and sometimes continuous with the matrix fabric. (specimen 87-12, cpl).
trail patterns continuous between grains in groups, but discontinuous with the surrounding fabrics. The patterns and geometries of these trails are often congruent with the patterns of microfolding developed in the fabric. Fabrics from secondary assemblages are seen in cartoon form in Fig. 4.18.

This rock is powerful evidence for the use of the Bell et al. model in interpreting microstructures. The Zwart criteria could be used to invoke pre-tectonic growth of albite (porphyroblasts folded by the shear bands and microfolds), syn-tectonic growth (inclusion trails continuous with the fabric and recording changing geometry from core to rim), and post-tectonic growth (highly complex inclusion trails). In this rock, attachment of such labels would result in a description of the deformation history that is reductionist in the extreme, as some grains clearly grew before deformation in one part of the rock, but prior to deformation in another part of the same rock. In the Bell et al. model, the porphyroblasts would be growing throughout a deformation that affected different parts of the rock at different times, those parts not undergoing shearing deformation being overgrown by albite, and the inclusion trail geometries resulting depending on whether the overgrown zone had yet undergone deformation or not. This rock therefore represents a snapshot of the deformational style and regime under way during the growth of porphyroblasts, this regime being dominated by isoclinal folding and shearing of pre-existing fabrics.

In the albite porphyroblast schists from South Bay, North of Tarbert, the matrices are generally highly micaceous and deformed. The inclusion trails in the porphyroblasts in these rocks are usually discontinuous with the matrix fabrics, implying much recrystallisation after growth of the porphyroblasts. However, geometries of microfolds in the matrices and in porphyroblasts are often very similar, and sometimes aligned the same way. As a result, the deformation associated with porphyroblast growth outlasted it, but continued in the same sense throughout.

Although it is clear that growth of albite porphyroblasts occurred during a deformational phase subsequent to the primary (B₁-D₁ and B₂a-D₂) deformation, and can therefore be considered a secondary event, the relationships of this growth event to the regional deformation history are not so clear. Watkins (1983) suggested that albite porphyroblasts grew during the D₃ deformation of Roberts and Treagus (1977). This deformation is probably equivalent to the B₂b of
Fig. 4.18 Summary cartoon of the development of the early stage secondary assemblages.
Watkins' timing of the growth of albite porphyroblast was based to a very large extent on a declaration, offered with little evidence, that the prograde metamorphism in the Balquidder area occurred between the D_2 and D_3 deformations of Harris et al. (1976). While recognising that the albite porphyroblasts grew in assemblages that overprinted the prograde Barrovian mineralogy, the deformation during which they grew is constrained to be D_4, by the contention of post-D_2 to syn-D_3 primary metamorphism. This was supported, not by textural evidence, but the coincidence of the exposure of the albite schists in the field with D_4 regional fold axes. As discussed in chapter 3, the timing of the primary regional metamorphism inferred by Watkins is likely to be wrong, and probably occurred during and immediately after D_1-D_2, as in the South West Highlands. This therefore means that the albite porphyroblast schists can in fact form during the D_3 of Harris et al. (1976), because this deformation would cause overprinting of the primary mineral assemblages. Greig (1985), however, suggested that albite porphyroblast growth occurred during the primary deformation, based on the similarity between some inclusion trail geometries in the cores of grains, and primary fabrics.

It is clear from the textures described above, that porphyroblast growth coincided with progressive crenulation, re-crystallisation, isoclinal folding and shearing of a planar, primary fabric. At no time can albite porphyroblast growth be linked with the primary deformation texturally. However, links with the monoformal folding associated with the B_2-b deformation of Roberts (1974) are also hard to draw as the inclusion trails and microfolds associated with porphyroblast growth are dominated by shearing and isoclinal folding. In addition, penetrative cleavages associated with B_2-b/D_4 folding are rare, and monoformal folds preserved as inclusion trails have not been observed.

Information pertaining to this problem has been derived from a series of thin sections cut from a plane normal to the pitching direction of monoformal folds in a very micaceous schist from South Bay. Conspicuous crenulation cleavages are developed locally in sheet silicate-rich layers, these being axial planar to monoformal folds of mineralogical layering (Fig. 4.19). The layering consists of albite porphyroblast-rich and sheet silicate-rich bands. A photomicrograph of thin section from this slab is shown in Fig. 4.20. From this, three observations are apparent:
Fig. 4.19 The cut and polished face of specimen 87-23, which preserves $D_1$ monoformal folds of mineralogical layering formed by the growth of albite porphyroblasts: the light layers are albite- and quartz-rich zones, while the darker layers are phyllosilicate-rich zones.
Fig. 4.20 Photomicrograph of one of the sections cut from 87-22: the crenulation cleavages that are axial planar to monoclinal folds of the mineralogical layering are clearly discontinuous with inclusion trails in the porphyroblasts, and must therefore have formed during a distinct deformational phase.
1. mineralogical layering is folded by the monoformal folds and locally developed axial planar crenulation cleavages cut the planar structure defined by this layering.
2. Inclusion trails in albite porphyroblasts are neither continuous nor congruent with the axial planar crenulation cleavage.
3. The crenulation cleavage is often refracted around albite porphyroblasts.

The folding of the albite-rich layering does not necessarily imply that this layering formed prior to the folding, as enhancement during porphyroblast growth might have caused albite to grow in layers already folded that were most favourable. The kind of mechanism suggested by Watkins (1983) for albite growth would have caused this to happen. However, all three of the above observations taken together indicate plainly that porphyroblast growth pre-dates the monoformal folding. Growth of the porphyroblasts cannot be synchronous with the monoformal folding as the inclusion trail fabrics are of a very different structural style to the axial planar crenulation cleavage and are discordant with it. For the same reasons, porphyroblast growth cannot post-date the monoformal folding and the crenulation cleavage.

On its own, the enveloping of the crenulation cleavage around the porphyroblasts could indicate syn-crenulation growth, the cleavages corresponding to zones of partitioned shearing deformation in the Bell et al. (1986) model. However, the other observations imply that this feature is in fact due to porphyroblast growth prior to monoformal folding, the cleavages refracting around the pre-existing porphyroblasts. The strongest evidence in favour of porphyroblast growth prior to the monoformal folding lies in the fact that the crenulation cleavage axial planar to monoformal folds always affects a fabric which demonstrably grew during, and after the growth of the albite porphyroblasts. As a result, porphyroblast growth can only have taken place prior to the monoformal folding. It must also have occurred after the primary deformation and during a folding event which appears to have been dominant in its influence on secondary metamorphic assemblages while not being immediately apparent in the regional patterns of folding.
4.2.3 Conclusions and Implications for the Deformation History in the South West Highlands:

It is clear that, as with the primary assemblages discussed in chapter 3, metamorphism and deformation are linked very closely. In the light of the implicit suggestion of the Bell et al. model that porphyroblast growth can only occur in the presence of deformation, this observation is entirely consistent and may indeed be repeated in most metamorphic belts. In the secondary assemblages in the South West Highlands, the link between deformation and metamorphism is particularly strong and is illustrated by the geometrical similarities between inclusion trails and matrix fabrics; indicating that the same deformational event gave rise to both sets of structures and that they both formed at the same time.

The first stage of the secondary metamorphic overprinting took the form of concentration of shearing deformation by re-activation of the primary cleavage (cf Bell et al. 1986). This was coincident with dissolution of primary and relict clastic mineralogy, especially clastic plagioclase feldspar which was recrystallised as porphyroblastic albite. Inclusion trails in these albites are straight, implying little rotation and de-activation of shear fabrics at this stage. The albite is also rectangular and aligned parallel to the surrounding matrix fabrics.

The next stages in the secondary deformation took the form of microfolding. In some rocks, porphyroblast growth ceased, while it continued in other assemblages. As a result, some porphyroblasts are displaced by buckle folding such that they are aligned at all times parallel to the limbs of the microfolds. In other assemblages, shearing, tighter microfolding and rotation of fabrics occurred giving rise to both complex inclusion trail patterns and matrix textures. Fig 4.21 shows cartoons of this deformation history and how it was dominated by shearing. Thus the deformational style during growth of albite porphyroblasts is dominated by shearing and rotation of planar fabrics.

The major conclusion of this section is that a regionally developed series of mineral assemblages grew during a pervasive deformational event that is restricted to the deeper structural levels in the post-D1-D2 nappe pile. Regional scale folds associated with this deformational event have not been recognised so far. This conclusion has many implications, some of which are discussed and amplified below.
Fig 4.21 Cartoons of the styles of shearing deformation seen in the fabrics of the secondary assemblages:
The major folds in the South West Highlands are either primary, that is, connected with the nappe-emplacement phase in the deformation history, or they are monoformal. Despite this, crenulation cleavages that are axial planar to monoformal folds are only weakly developed at best, and often absent. The growth of regionally developed secondary metamorphic assemblages during a deformational event after nappe emplacement but prior to monoformal folding would give a similar picture to the Central Highlands where, as noted in chapter 3, prograde assemblages grew during the D₃ deformation of Harris et al. (1976). Mendum (1988, pers. comm.) described field observations of various stages of D₃ folding from other parts of the Dalradian which resembled the evolution of folds recognised here. The folds developed progressively from open to isoclinal styles. Mendum (pers. comm.) also interpreted the texture in specimen 87-12 as resembling D₃ styles more closely than D₄ folding.

If the albite schist assemblages did grow at the same time as the D₃ deformation of Harris et al. (1976), the secondary metamorphism might be a response to the same regional deformation as was related to the Barrovian metamorphism in the Central Highlands; that is, they are equivalent events in the respective metamorphic histories of the South West and Central Highlands, occurring at about the same time. It is notable that on Fig. 4.8, the end of the zone of outcrop of the albite porphyroblast schists to the north-east coincides with the widening of the garnet zone to the north-east of the Cruachan line.

4.3 The Secondary Metamorphism; Assemblages and Reactions:

Having defined the structural style and framework during secondary deformation, it is now time to present information on the later overprinting mineralogy which formed at this time. So far, enough information has been described to derive the deformation style and the textural evolution of the secondary assemblages; in that the presence of complex fabrics, the replacement of AFM phases with chlorite, and the growth of albite porphyroblasts have been itemised. Clearly, this information is insufficient to derive details on the petrogenesis of these assemblages, rather than their formation in a strictly structural sense. This section is therefore designed firstly to expand the petrographic database, then to discuss the reactions responsible for the growth of the secondary metamorphic assemblages, based on the petrography. These
reactions are those which tend to cause changes in mineralogy; "cryptic" changes in mineral chemistry and the continuous reactions responsible will be discussed in the succeeding section.

4.3.1 Assemblages; Petrographic Evidence on the Nature of the Secondary Metamorphism:

The assemblages developed during metamorphism associated texturally with the secondary deformation are of four types: carbonates, low modal chlorite pelites, high modal chlorite pelites and k-feldspar-bearing pelites. Rocks representing each of these assemblage types will be described in turn.

4.3.1.1 Secondary Carbonates:

Graham et al. (1983) and Greig (1985) describe secondary, overprinting carbonate assemblages from South Bay, near Tarbert, exposed as metre-scale bands weathering a rusty-red colour, separated by primary, grey-weathering bands from amphibolite horizons. Typical assemblages are:

\[ qz + pheng + dol-ank + ksp + rut \pm chl \pm bi \pm ab \]

(abbreviations in this chapter are the same as in chapter 3)

Graham et al. (1983) use the co-existence of chlorite and k-feldspar to assign temperature conditions close to those of the lower Greenschist Facies, as a result of reversal of the reaction for the growth of biotite in k-feldspar bearing pelites:

\[ chl + ksp = bi + pheng + qz + \text{fluid} \quad (1) \]

(Mather 1970, Miyashiro and Shido 1985, Massonne and Schreyer 1987, chapter 5)

The secondary carbonate assemblages are restricted in exposure to the Loch Tay Limestone. Graham et al. (1983) describe textural evidence showing that these assemblages are secondary, including the pseudomorphing of sphene by rutile and carbonate and the replacement of clininozoisite by carbonate. Analyses for oxygen and carbon isotopes in these rocks by Greig (1985) confirm that the fluid phase was distinct from that which infiltrated other carbonates with primary, higher
temperature mineralogy (Fig. 4.22, Greig 1985). While the carbon isotope values are similar in both sets of rocks, they define different trends when plotted against the extent of decarbonation (as measured qualitatively by the mineral assemblages present). The oxygen isotope values vary by up to 20 per mil, with retrograde carbonates having $\delta^{18}O$ values between $+25$ and $+30$ per mil, compared to between 5 and 10 per mil. in the primary carbonates.

Graham et al. conclude that the secondary infiltrating fluid had an $XCO_2$ value of at least 0.02, based on the P-T conditions calculated by these authors, as well as on the stable co-existence of phengite, dolomite, rutile, quartz and k-feldspar.

4.3.1.2 Low Modal Chlorite Pelites:

In and around the Tarbert area, the Green Beds are exposed. These, although they are metasedimentary, have a volcaniclastic component, which probably affected their bulk chemistry and, as a result, their metamorphic history. Most of these rocks have fabrics crenulated to varying extents and are rich in epidote and olive-green biotite, while chlorite is usually rare and often absent. Porphyroblastic albite is often present, particularly in the more quartzitic assemblages. Typical assemblages are:

$$qz + pheng + bi + ep/zo + ab + mt + ilm$$

The biotites are a very distinctive olive green colour but showing pleiochroism to a weaker yellow-brown. In some, highly micaceous assemblages, biotite of this colour is concentrated along crenulations of the mica fabric, as well as forming rims around ore grains. Similar types of biotite are described by Verschure et al. (1980) and Chinner (1960). The rocks are also entirely garnet-absent, even though they are found in areas which reached high grades during the primary metamorphism.

While Verschure et al. (1980) point out that the first biotite to appear in a prograde metamorphic sequence is often the colour seen here, implying that this colour is diagnostic of lowest biotite zone temperatures, Chinner (1960) also show that the oxygen fugacity, $fO_2$, is also influential, with high $fO_2$ leading to growth of green biotite. As a result, biotite of the kind seen in these rocks seems to have been stable during the secondary metamorphism, and probably grew at this time.
Fig. 4.22 $\delta^{13}C$ and $\delta^{18}O$ values from analyses of primary and secondary carbonates from Knapdale: The secondary carbonates from South Bay are the group III analyses in the figure, the other two groups are all primary assemblages (from Greig 1985).
Reasons for the growth of this type of biotite will be considered in section 4.4, with a view to estimating qualitatively the fO₂ conditions and the influences these had on the mineral chemistry and phase relations.

4.3.1.3 High-Modal-Chlorite Pelitic Assemblages:

These assemblages are widely developed, being found throughout the Northern Kintyre area, mainly in the Beinn Bheula Schists. Most of the rocks described in section 4.2 are of this type. Typical assemblages are:

\[
\text{qz} + \text{pheng} + \text{chl} + \text{ab} + \text{mag} \pm \text{gt} \\
\pm \text{sph} \pm \text{ep/zo} \pm \text{bi} \pm \text{cc}
\]

As has already been discussed in section 4.2, the phengite and chlorite often occurs in complex fabrics and geometric patterns, while the albite is usually porphyroblastic, but of varying habit and relationships with the matrix. The chlorite is found either as intergrowths with the phengite, or as replacements of biotite. It is always abundant and often coarse grained. Biotite is rare, usually occurring as intergrowths and remnants within chlorite. The pleiochroic schemes of co-existing biotite and chlorite in these rocks is such that they both have very similar weak yellow-brown colours when aligned in a north-south direction under the microscope. In alignments normal to this, the chlorite is a strong blue-green while the biotite is a mid to dark brown. Chlorite in rocks with no biotite have a similar pleiochroic scheme. This is possibly due to fine-scale intergrowth of the two phases. While the olive-green biotites described previously are either stable during, or are product phases of, the secondary metamorphism, biotites in the high modal chlorite assemblages are invariably breaking down; they are unstable and are reactants. Contrasts in the biotites, and the phases co-existing with them, are discussed further in section 4.4 below.

Garnet usually occurs as small, pristine euhedra, both as inclusions in albite porphyroblasts, and in the matrix, even of rocks that are completely biotite-absent, and which have pervasively recrystallised fabrics. Garnet-bearing assemblages also have high modes of oxide phases.
4.3.1.4 K-feldspar-bearing pelites:

K-feldspar as a secondary phase is restricted to the Stonefield Schists which outcrop at South Bay. In these rocks it occurs as rims on albite porphyroblasts, but only where these are in contact with sheet silicate-rich zones. (eg Fig. 4.16). Typical assemblages are

\[ \text{pheng} + \text{ab} + \text{chl} + \text{qz} \pm \text{bi} \pm \text{gt} \pm \text{ksp} \pm \text{sph} \pm \text{rut} \pm \text{cc} \]

These rocks are very rich in phengite and have a mineral layering defined by quartz-rich zones, albite segregations, and mica- and chlorite-rich bands.

While usually occurring as a discrete rim on porphyroblastic albite, k-feldspar is also found as very fine-scale intergrowths with albite forming rust-coloured rims on grains in albite-rich segregations. In most of these assemblages, almandine-grossular garnets are found as remnants in the matrix and as inclusions in albite porphyroblasts. The inclusions are usually pristine, while the grains in the matrix are often altered and rimmed by chlorite.

Sometimes, the k-feldspar rims are very broad while the albite grains are small and ragged (Figs 4.23 and 4.24). In this rock, CA 17, both garnet and biotite are entirely absent, while chlorite and phengite are intergrown intimately. A reaction of the form:

\[ \text{bi} + \text{pheng}(1) + \text{fluid} = \text{chl} + \text{pheng} (2) + \text{ksp} + \text{qz} \]  

is probably responsible for the growth of these assemblages. The other assemblages already described with thinner k-feldspar rims usually contain biotite. This is often preserved in low strain zones in the phengite-rich fabric, or close to albite porphyroblasts, which, as would be expected, seem to have acted as strain shadows. In all k-feldspar bearing assemblages, reactions of the form given by (2) or (3) would have operated, but have gone closest to completion in 71-3. The k-feldspar-bearing assemblages therefore represent the latest stages in the secondary metamorphism, with the k-feldspar and chlorite replacing biotite and garnet, and the overgrowing and eventual breakdown of albite porphyroblasts.

While garnet seems to have been stable during the growth of albite
Fig. 4.23 The final stage in the textural evolution of the secondary assemblages: k-feldspar rims replace albites which are preserved as remnants. The assemblage is chlorite-rich and biotite-free (specimen CA 16, cpl)
Fig. 4.24 As Fig. 4.23, but in ppl. The matrix consists of phengite (paler) and chlorite (darker) intergrown intimately.
porphyroblasts, other phases, especially sphene, were not, even when entirely surrounded by albite. The only garnets to be replaced by chlorite are the large euhedral grains not engulfed by albite. There are two possible reasons for these apparently contradictory observations:

1. the kinetics of the reaction sph + CO2 = rut + cc are faster than the reaction for the breakdown of garnet to chlorite.
2. The rocks were sufficiently warm for garnet to remain stable as the albite porphyroblasts grew, and the infiltrating fluid was sufficiently rich in CO2 to cause the breakdown of sphene.

At this stage in the thesis, not enough information has been presented to decide on the possibilities just itemised. The second possibility would be easier to confirm or refute in principle, but would require that cooling rates from peak metamorphic temperatures were relatively slow, such that the lower temperature stability limit of garnet was not exceeded, or overstepped by a significant amount. The highest grade primary assemblages are formed at Tarbert and Northern Kintyre (chapters 3 and 5) where the albite porphyroblast schists are concentrated, so the rocks in this area would have the furthest to cool before cooling below the lower temperature stability limit of garnet.

4.3.1.5 Summary:

The secondary metamorphic assemblages, as with the fabrics, record a history of progressive overprinting of primary mineralogy. As a result, the assemblages buffering the phengite chemistry have changed and so equivalent changes in the phengite chemistry must be expected. The secondary assemblages depend, however, on the original rock type and, by inference, bulk composition, with the k-feldspar-bearing assemblages restricted to the highly micaceous Stonefield Schists in South Bay, the green biotite-bearing rocks to what were originally volcaniclastic horizons, and the high modal chlorite assemblages restricted to the Beinn Bheula Schists. Bulk rock chemistry has therefore played an important role in deciding which mineral assemblages are preserved.

The secondary metamorphic assemblages are often anomalous in that biotite and garnet are often stable, but never co-exist. Each of the secondary assemblage types is restricted to specific protoliths and stratigraphic horizons, leading to the conclusion that the bulk chemistry of these rocks was instrumental in deciding the respective stabilities and the compositions of chlorite, biotite and garnet.
The secondary metamorphism consisted of two main stages: the earlier stage being the growth of albite porphyroblasts, described in detail in section 4.2, and the second being more limited and concerning the breakdown of biotite to chlorite and k-feldspar. The earlier stages of the secondary metamorphism therefore affected all the pelitic assemblages while the later stages were restricted to the k-feldspar-bearing secondary assemblages.

4.4 Secondary Metamorphic Assemblages; Phase Equilibria and Mineral Chemistry:

This section is devoted to the derivation of the changes in mineral compositions that occurred as a result of secondary, overprinting metamorphism. In addition, the effects of Fe/Mg ratios, Mn abundances and fO₂ conditions on the stabilities of chlorite, biotite and garnet co-existing with phengite will be considered.

The changes in chemistry to be detailed will be synthesised with the petrographic evidence on the extent of overprinting of primary metamorphic mineralogy to produce a time-integrated picture of the secondary metamorphism. As with section 3.2, the phase relations of these assemblages will be shown primarily on the AK'F (K' = k-feldspar) and the A'FM (A' = Al₂O₃ - K₂O) composition-paragenesis diagrams. The usages and limitations of these projections are discussed in section 3.2. As with the prograde assemblages, k-feldspar is not a "ubiquitous" phase, so the A'FM projections will not be rigorous.

4.4.1 Low Modal Chlorite Pelites:

Mineral analyses of phengite, biotite and the oxide phases have been made in one of these assemblages sample 84-4 from the north coast of West Loch Tarbert. Because chlorite is absent, this assemblage will not buffer the phengite chemistry. Table 4.1 is a presentation of analyses from this assemblage. Oxide phases are either almost pure magnetite (Fe³⁺/(Fe²⁺ + Fe³⁺) = 0.64-0.667) or they are very rich in titanium. Thus, this assemblage is characterised by co-existing magnetite and rutile. The phengites contain 3.25 to 3.3 Si p.f.u. (based on 11 oxygens) and Mg/(Fe + Mg) of 0.45-0.5 (all Fe as Fe²⁺). The biotites contain 1.8 to 2.4 weight %
Table 4.1: Representative analyses of minerals from specimen 84-4, a low modal chlorite pelitic assemblage:

<table>
<thead>
<tr>
<th>Wt. % oxides</th>
<th>Ti-oxides</th>
<th>Fe-oxides</th>
<th>Biotites</th>
<th>Phengites</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1.77</td>
<td>1.08</td>
<td>0.00</td>
<td>0.63</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.99</td>
<td>0.9</td>
<td>0.05</td>
<td>0.81</td>
</tr>
<tr>
<td>TiO₂</td>
<td>49.87</td>
<td>84.99</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>MgO</td>
<td>1.67</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>MnO</td>
<td>0.41</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>21.43</td>
<td>5.07</td>
<td>19.20</td>
<td>20.69</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.00</td>
<td>0.00</td>
<td>42.78</td>
<td>41.58</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>76.14</td>
<td>92.07</td>
<td>62.11</td>
<td>63.78</td>
</tr>
</tbody>
</table>

FeO is for total iron in the analyses marked (*).

Table 4.2: Analyses of brown biotites from different phengite-biotite-chlorite bearing pelitic assemblages:

<table>
<thead>
<tr>
<th>Wt. % oxides</th>
<th>85-23</th>
<th>71-26</th>
<th>84-22</th>
<th>86-8</th>
<th>86-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>36.76</td>
<td>34.66</td>
<td>34.33</td>
<td>36.52</td>
<td>35.66</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.40</td>
<td>14.98</td>
<td>17.53</td>
<td>17.39</td>
<td>16.51</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.26</td>
<td>1.92</td>
<td>2.25</td>
<td>1.74</td>
<td>2.12</td>
</tr>
<tr>
<td>MgO</td>
<td>6.19</td>
<td>10.24</td>
<td>7.31</td>
<td>7.86</td>
<td>8.92</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.20</td>
<td>0.15</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>FeO</td>
<td>19.04</td>
<td>20.98</td>
<td>23.06</td>
<td>23.08</td>
<td>21.99</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
<td>0.16</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.11</td>
<td>0.10</td>
<td>0.06</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.08</td>
<td>8.29</td>
<td>9.01</td>
<td>8.74</td>
<td>9.40</td>
</tr>
<tr>
<td>Σvi</td>
<td>2.88</td>
<td>2.97</td>
<td>2.88</td>
<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>Total</td>
<td>90.97</td>
<td>91.53</td>
<td>93.71</td>
<td>95.67</td>
<td>94.91</td>
</tr>
</tbody>
</table>

FeO is for total iron in all the analyses.
TiO₂, they are depleted in K₂O to varying extents, and have Mg/(Fe+Mg) of about 0.41 to 0.42 (all Fe as Fe⁺). AK’F and A’FM projections for this assemblage are shown on Fig. 4.26.

The major anomaly in this assemblage is the absence of chlorite and the growth of biotite as a secondary phase. Chinner (1960) suggested that variations in oxygen fugacity (fO₂) during metamorphism can affect the stability relations and chemistry of chlorite, biotite and garnet. Colour variations in biotite are usually ascribed to variations in TiO₂ contents, with high Fe₂O₃/TiO₂ ratios giving a green colour (Hayama 1959, Deer et al. 1966, p. 213). The biotites in this assemblage have a green colour and the oxide phases are rich in TiO₂. In addition, oxide grains are sometimes mantled by biotite. Chinner (1960) found that green biotites with reduced TiO₂ and increased Fe₂O₃ were present in sillimanite zone assemblages inferred to have undergone metamorphism under high fO₂ conditions by the presence of haematite and high whole-rock Fe₂O₃ contents.

The experimental data of Buddington and Lindsley (1964) and Spencer and Lindsley (1981) show that at temperatures below about 550 °C, the ranges of solid solution in oxides is very low, thus at garnet zone temperatures, or lower, the oxide phases that grow will have close to endmember compositions and will not therefore be good indicators of fO₂ conditions.

In the absence of wet chemical analysis, the amount of Fe³⁺ in any iron-bearing silicate is difficult to determine and depends on assumptions relating to stoichiometry and site occupancy. Applying the recalculation scheme of Droop (1987) to the olive-green biotites results in negative abundances of Fe³⁺ because all the biotites analysed have vacancies in the octahedral sites (table 4.1). Based on what is known about other green-biotite bearing assemblages, it seems reasonable to suppose that the biotites in 84-4 are enriched in Fe³⁺ relative to biotites in other assemblages. In the analyses of Chinner (1960, table 5) the brown biotites have Fe₂O₃/TiO₂ ratios ranging from 0.5 to 1.15, while the green biotites, found in oxidised rocks have Fe₂O₃/TiO₂ ratios ranging from 1.67 to 2.65.

Chemical data for brown biotites from assemblages in the South West Highlands are presented in table 4.2. Samples 85-23 and 86-10 are garnet zone garnet-absent pelites, 86-8 is a garnet-bearing assemblage, 84-22 is an albite porphyroblast schist from South Bay and 71-26 is a biotite-bearing amphibolite.
none of these biotites are the TiO$_2$ contents significantly different from those of the green biotites in 84-4. In addition, none of them have octahedral site occupancies greater than three. One apparent difference is that Mg/(Fe$^{II}$ + Mg) ratios in the green biotites (where all Fe is taken as Fe$^{II}$, in table 4.2) are greater than those in the brown biotites, including the garnet-absent assemblages. A similar trend was also noted by Chinner (1960). It would seem that at lower grade, biotite may act as a sensitive, but as yet, uncalibrated, indicator of fO$_2$ conditions of metamorphism. Varying fO$_2$ may also affect the Mg/(Fe$^2$ + Mg) ratios, which in turn will affect the stability relations of co-existing ferro-magnesian phases.

Another chlorite-absent assemblage for which mineral chemical data are available is 87-11CMG, an epidote-phengite-Mg-biotite-albite-quartz calc-schist from South Bay. A planar fabric defined by phengite, biotite and quartz, with equant epidote grains, is overgrown by poikiloblastic biotite, phengite and albite. The biotite is very Mg-rich, as is the phengite, which is also Si-rich. A'FM and A'KF diagrams for both 87-11CMG and 84-4 are shown in Fig. 4.26. Both these diagrams show how Si-rich the phengites in these assemblages are in relation to those in chlorite-bearing assemblages (section 3.2, and below, 4.4.2). In chapter 3, it was shown that biotite is stabilised preferentially at given P-T conditions in Si-rich bulk rocks, and it was suggested that Fe-rich bulk rock compositions will also stabilise biotite preferentially to Mg-rich bulk rocks. The two assemblages discussed here show that if the Al/Si ratio of a bulk rock is sufficiently high, biotite will be stable, and chlorite unstable, even when the bulk rock chemistry is Mg-rich.

4.4.2 High Modal Chlorite Pelites:

These assemblages fall into two groups: garnet-absent and garnet-bearing assemblages. The garnets are almost always small and euhedral and are all spessartine-rich. Watkins (1983) and Chinner (1960) both recognised garnets of similar habits and chemistry. The oxides are usually pure magnetite, and the phengites show wide variability, both within an assemblage and between assemblages. AK'F and A'FM diagrams are shown for some of these assemblages in Figs 4.25 and 4.27.
Fig. 4.25 A'FM diagrams for secondary assemblages: (a) garnet-bearing and (b) garnet-absent pelites:
Fig. 4.26 (a) AK'F and (b) AFM (from k-feldspar) projections for 84-4 and 87-11CMG two low modal chlorite secondary assemblages:
4.4.2.1 A'FM and AK'F Relations:

The assemblages 87-11 and 85-12 are both spessartine-rich garnet-bearing and 85-12 also bears biotite. 87-06 also contains garnets, but only rarely and as inclusions in albite porphyroblasts. The other assemblages are all garnet-absent, epidote-bearing, and have high modal chlorite.

The phengite in 87-06 is marginally more celadonitic and magnesian than that of 87-11. In comparison, 87-07 is garnet absent, has similarly celadonitic but slightly more magnesian phengite than in 87-06. All the relationships described are shown in the two phengite composition diagrams (Figs 4.28, 4.29). Obviously, in a non-buffering assemblage the Fe/Mg ratios of the phases present will depend ultimately on the bulk rock Fe/Mg ratios, such that high Fe contents favour the growth of higher grade mineral assemblages at given P-T conditions. All these conclusions, again, are not new (eg A.B. Thompson 1976) and are similar to those drawn in section 3.2 for the primary assemblages.

To conclude, therefore, the phengite chemistry in the secondary assemblages depends on the phases with which it co-exists. These in turn depend on bulk rock composition. The factors causing and influencing the growth of spessartine-rich garnet are examined next.

4.4.3 The Growth of Spessartine-Rich Garnet:

In most Barrovian metamorphic terrains, almandine-grossular-rich garnet is developed as an index mineral at grades above those of the first appearance of biotite. In some "progressive" sequences, though, spessartine-rich garnet is developed at grades lower than the first appearance of biotite, an example being the Sanbagawa Belt, Japan (Kurata and Banno 1974). In what was an impressive petrological study (especially because it was carried out in the days before the now-ubiquitous microprobe), Chinner (1960) showed how spessartine-rich garnet is stable at lower temperatures than biotite, in oxidised and Mn-rich rocks. These predictions were based on the following relationships:

\[(X\text{-Mn})_{gt} > (X\text{-Mn})_{chl} > (X\text{-Mn})_{bi}\]
\[(X\text{-Fe})_{gt} > (X\text{-Fe})_{bi} > (X\text{-Mn})_{chl}\]
Fig. 4.27 AK'F diagrams for secondary assemblages: (a) garnet-bearing and (b) garnet-absent pelites:
Fig. 4.28 Schematic phengite composition diagram after J.B. Thompson (1979), for assemblages metamorphosed under P-T-X-fO2 environments in which garnet is unstable:
Fig. 4.29 Schematic phengite composition diagram for assemblages metamorphosed under environments in which garnet is stable:

Both of Figs 4.28 and 4.29 are consistent with the chemistry seen and described in the text and shown in previous figures, but Fig. 4.29 allows Mg-richer phengite to co-exist with biotite only than Fig. 4.28 and is therefore more consistent with 87-11CMG.
Thus, in Mn-rich rocks, the reaction

$$\text{pheng (1) + qz + chl = gt + pheng (2) + fluid}$$

would occur at lower temperatures than the "Thompson" reaction for the growth of biotite and garnet:

$$\text{pheng + chl + qz = bi + gt + fluid.}$$

As a direct follow-up to this study, Hsu (1968) carried out a comprehensive series of garnet synthesis experiments under varying $P_H_2O-T-fO_2$ conditions, and showed that the lower temperature stability limit of spessartine was about 100 °C lower than that of almandine, and that as fO$_2$ increased, the P-T space occupied by almandine decreased at both low and high temperatures. While the lower temperature stability limit of almandine increased with increasing fO$_2$, that of spessartine did not to the same extent (Fig. 4.30).

The studies of Chinner and Hsu provide an answer to the problem of how garnet can be stable when biotite is not. The garnets in these rocks contain about 25-30% spessartine (table 4.3). Phengites and chlorites from garnet-bearing and garnet-absent high modal chlorite pelites are shown plotted on Mn-Mg-Fe diagrams in Fig 4.31. This diagram shows that the phases in garnet-bearing assemblages are Mn-richer than those in garnet-absent assemblages. 87-11 has the Mn-richest chlorite and is garnet-bearing while 86-5 and 86-6 are garnet-absent and have Mn-poor chlorite. Therefore, although bulk rock Fe/Mg ratios decide at what temperatures garnet will grow, the growth of this phase is favoured strongly if the bulk rock is also Mn-rich.

The other petrographic observation of note in these assemblages is the often high mode of oxide phases. In the rocks analysed, these are pure magnetite and therefore indicate high fO$_2$ conditions, though these are not well constrained due to the relatively low temperatures of metamorphism of these assemblages. Watkins (1983, 1984) found identical assemblages in the same stratigraphic horizon in the west-Central Highlands and showed that the lithologies were oxidised relative to surrounding rocks. The oxidised lithologies recognised by Chinner (1960) in the east-Central Highlands are also in the same stratigraphic
Fig. 4.30 Almandine-spessartine phase relations: spessartine is stable at lower temperatures, and at higher fO2, than almandine (from Hsu 1968).
Fig. 4.31 Mg-Mn-Fe diagram for phengites and chlorites from the same assemblages as plotted in Fig. 4.26: (a) garnet-bearing and (b) garnet-absent assemblages: chlorites and phengites in garnet-bearing assemblages tend to be Mn-richer than those in garnet-absent assemblages.
position. I infer, therefore, that these assemblages formed under highly oxidising conditions. The major implication of this conclusion is that unambiguous but qualitative information on \( f_{O_2} \) conditions of metamorphism in lower grade assemblages can be derived simply from the mineral assemblages present without recourse to the iron oxide phases which are uninformative at low to medium grades.

Both types of secondary assemblage described so far are restricted to a particular protolith, usually defining a stratigraphic horizon, and also resulting in the widely differing assemblages produced in the same phase in the metamorphic history of the South West Highlands. The next subsection describes the mineral chemistry of assemblages which preserve the later stages of the secondary metamorphism, and are also restricted to a specific protolith, also defining a stratigraphic horizon.

### 4.4.4 The k-Feldspar-Bearing Pelites:

The k-feldspar-bearing secondary assemblages are restricted to the Stonefield Schists which crop out to the north of Tarbert, particularly at South Bay. They are albite-porphyroblastic but are distinguished from the other albite schists by the presence of k-feldspar rims of varying thicknesses growing on the albite porphyroblasts. They preserve the latest fabrics formed, hence the latest stages in the secondary metamorphism. No other secondary assemblages found are k-feldspar-bearing, and few of them have matrix fabrics as discordant with the inclusion trails in the porphyroblasts as these assemblages. These assemblages also preserve remnants of the primary Barrovian mineralogy, especially almandine-grossular garnet. These rocks are therefore not as oxidising as the other secondary pelitic assemblages.

#### 4.4.4.1 Mineral Chemistry:

The phengites in the k-feldspar-bearing assemblages are depleted in Si in comparison with the phengites in the other secondary assemblages. This is despite the influence on phengite chemistry predicted by J.B. Thompson's phengite composition diagrams (Fig. 4.28 and 4.29, see also section 3.2 and Miyashiro and Shido 1985) which suggests that phengites co-existing with k-feldspar should be Si-enriched. \( Mg/(Fe+Mg) \) ratios are typically 0.48 to 0.51 in all the
assemblages, while Si p.f.u. varies from 3.2 to 3.3 (tables 4.3 and 4.4). In rock no. 71-3, which is biotite-absent and has thick k-feldspar rims growing on ragged albite remnants, the phengites have lower Si p.f.u. than in the other assemblages, with values of between 3.08 and 3.2. In addition, this phengite is enriched in Na and depleted in K. In all the phengites, there is very little depletion of alkalis. Phengite inclusions in all these rocks are Si-richer than in the matrix.

All the biotites in these rocks are brown and have between 1.7 and 2.2 wt.% TiO2. As the biotites are brown coloured, they are inferred to have formed under more reducing conditions than the low modal chlorite assemblages already described. Support for this comes from the complete absence of spessartine-rich garnet and the presence of relics of almandine-grossular rich garnet, which grew during the primary metamorphism. The Mg/(Fe+Mg) ratios in these biotites range between 0.36 and 0.38. In these assemblages, biotite is always being replaced by chlorite, and is absent from specimen 71-3.

The chlorites within an assemblage are usually chemically homogeneous with respect to Al and Si contents, but less so with respect to Mg and Fe contents. There is, however, some variation between assemblages in Al contents, with the chlorites in 71-3 being Al-richer than those in other assemblages. Mg/(Fe+Mg) ratios vary between 0.40 and 0.41, but those in 71-3, in which biotite is absent, are less than 0.38.

The feldspar in these assemblages is either almost pure albite, or almost pure k-felspar. Although Watkins (1983) reported CaO contents of a "few wt. %" on the margins of porphyroblasts, no increase of such a magnitude is seen in the Knapdale assemblages.

To summarise the mineral chemistries of the phases making up the k-feldspar-bearing assemblages, most phases have similar chemistries throughout the assemblages analysed, with most variation occurring in Mg/Fe ratios in phengite and chlorite. In none of the phases analysed is there evidence of oxidising metamorphic conditions, and the assemblages developed do not show the "anomalies" found in the other secondary assemblages. The one anomalous feature of these rocks is the co-existence of Al-enriched phengite with k-feldspar, whose modal abundance increases with the Al-enrichment.
### Table 4.3: Representative mineral analyses from k-feldspar-bearing secondary pelitic assemblages; phengites:

<table>
<thead>
<tr>
<th>Wt. % oxides</th>
<th>71-1</th>
<th>71-3</th>
<th>84-22</th>
<th>71-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.19</td>
<td>47.46</td>
<td>46.23</td>
<td>46.84</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>30.75</td>
<td>30.64</td>
<td>35.51</td>
<td>35.30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.30</td>
<td>0.33</td>
<td>0.26</td>
<td>0.30</td>
</tr>
<tr>
<td>MgO</td>
<td>1.95</td>
<td>1.91</td>
<td>0.67</td>
<td>0.82</td>
</tr>
<tr>
<td>MnO</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>3.46</td>
<td>3.29</td>
<td>1.21</td>
<td>1.49</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.48</td>
<td>0.53</td>
<td>0.85</td>
<td>1.36</td>
</tr>
<tr>
<td>K₂O</td>
<td>10.22</td>
<td>10.10</td>
<td>9.87</td>
<td>9.24</td>
</tr>
<tr>
<td>Total</td>
<td>95.35</td>
<td>94.27</td>
<td>94.60</td>
<td>95.35</td>
</tr>
<tr>
<td>100.Mg</td>
<td>50.1</td>
<td>50.1</td>
<td>49.7</td>
<td>49.5</td>
</tr>
</tbody>
</table>

FeO is for total iron in all the analyses.

### Table 4.4: Representative mineral analyses from k-feldspar-bearing secondary pelitic assemblages; biotites and chlorites:

<table>
<thead>
<tr>
<th>Wt. % oxides</th>
<th>Bi-Chl</th>
<th>Bi-Chl</th>
<th>Bi-Chl</th>
<th>Bi-Chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.84</td>
<td>24.14</td>
<td>23.20</td>
<td>34.33</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.59</td>
<td>21.73</td>
<td>22.43</td>
<td>17.53</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.95</td>
<td>0.11</td>
<td>0.06</td>
<td>2.25</td>
</tr>
<tr>
<td>MgO</td>
<td>7.79</td>
<td>11.45</td>
<td>10.56</td>
<td>7.31</td>
</tr>
<tr>
<td>MnO</td>
<td>0.21</td>
<td>0.24</td>
<td>0.27</td>
<td>0.15</td>
</tr>
<tr>
<td>FeO</td>
<td>22.97</td>
<td>29.17</td>
<td>30.16</td>
<td>23.06</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.37</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>8.41</td>
<td>0.00</td>
<td>0.00</td>
<td>9.01</td>
</tr>
<tr>
<td>Total</td>
<td>95.18</td>
<td>86.84</td>
<td>86.68</td>
<td>93.71</td>
</tr>
<tr>
<td>100.Mg</td>
<td>37.7</td>
<td>41.2</td>
<td>38.4</td>
<td>36.1</td>
</tr>
</tbody>
</table>

FeO is for total iron in all the analyses.
4.4.4.2 Phase Relations in K-Feldspar-Bearing Assemblages:

As with all the other pelitic assemblages described in this thesis, the phase relations of the k-feldspar-bearing assemblages are to be illustrated using the AK'F and A'FM diagrams. Despite the presence of k-feldspar in these assemblages, they show clear petrographic evidence of disequilibrium, with the k-feldspar growing as a late phase. Thus, the A'FM projection from k-feldspar will be, again, non-rigourous.

A'FM and AK'F plots of a number of k-feldspar-bearing assemblages are shown on Figs 4.32 and 4.33. These diagrams show all the mineral chemical features described above, with most assemblages being similar to one another, with the conspicuous exception of 71-3. Each one of the k-feldspar-bearing assemblages has probably undergone Al-enrichment in its phengite, because phengite inclusions in albite porphyroblasts have lower Al contents than the matrix phengites. The chlorites in these assemblages show a similar trend with chlorite in 71-3 again having the highest Al contents. As a result, these assemblages chart changes in phengites and chlorites related to the textures, and imply that Al has been enriched as the secondary metamorphism became more pervasive. These changes are summarised in Fig. 4.34 and will be discussed further in section 5.1.

These conclusions do not necessarily imply that the biotite-absent assemblages preserve a later stage in the evolution of these assemblages; they show, again, how bulk rock chemistry apparently influences the assemblages that are developed. Again, lower temperature-stable mineralogy is favoured in Al-rich bulk rock compositions. However, it will be shown in section 5.1 that the Al-contents in phengites co-existing with chlorite and k-feldspar increase with decreasing temperature, the reverse of what has been shown to occur in the primary biotite-chlorite-bearing assemblages. The Al-enrichment seen in these assemblages with progress of the secondary, overprinting metamorphism is therefore either due to varying bulk rock chemistries, or to the biotite-absent assemblages preserving later stages in time of the secondary metamorphism. These two possibilities cannot be distinguished on the information available at present; the overprinting assemblages cannot be shown to have grown simultaneously, or at different times, from the textures, unlike what is possible for the primary assemblages, and there are no bulk rock analyses available.
Fig. 4.32 A FM projection for k-feldspar-bearing pelites: the phengites are richer in Al than phengites in the other secondary assemblages, and have been enriched in Al during the secondary metamorphism.
Fig. 4.33 AK'F projection for k-feldspar-bearing pelites: the Al-enrichment in phengite that has occurred during overprinting of the primary assemblage with chlorite and k-feldspar is shown by the phengite inclusions and the high Al contents of chlorites and phengites in 71-3.
Fig. 4.34 Summary of the phase topological changes in the k-feldspar-bearing secondary assemblages: phengites become Al-richer in assemblages that are retrogressed further; this Al-enrichment is associated with the relative modal abundances of k-feldspar, chlorite and biotite, the k-feldspar-rich and biotite-poor assemblage, 71-1, having Al-richer phengite.
4.5 Conclusions and Implications:

This chapter was in two parts, the first dealing with the textural evolution of the secondary metamorphic assemblages, and the implications for the deformational history of the South West Highlands, and the second dealing with the metamorphic and mineral chemical evolution of the assemblages. This section will summarise the more important of the conclusions drawn in this chapter and the implications that these have for the regional metamorphic history of the South West Highlands.

4.5.1 Deformation:

The secondary metamorphism was a response to pervasive regional deformation that affected the deepest structural levels of the thickened crust. The textures developed in the secondary assemblages indicate that this deformation post-dates the primary deformation associated with the formation and emplacement of the Tay Nappe but pre-dates the secondary folding associated with the Tarbert Monoform and the Cowal Antiform. Thus, an additional phase of regional deformation needs to be invoked for the South West Highlands, for which no regional scale folds have yet been recognised.

The relative timing of this newly recognised deformation is equivalent to the D3 deformation seen in the Central Highlands, during which the prograde Barrovian metamorphism occurred. The structural styles of the early stages in the secondary deformation, during which the albite porphyroblast schists were formed, are very similar to the styles of D3 deformation in the Central Highlands, thus suggesting that the albite schist growth event is equivalent to the Barrovian metamorphism in the Central Highlands, the two different sets of assemblages being two different responses to the same deformational event. The regional exposure of the secondary assemblages coincides with the narrow garnet zone to the south-west of the Balquidder area, and terminates close to the position of the Cruachan Lineament. As a result, the differing properties of the deep crust already postulated for the South West Highlands in comparison with the Central Highlands may have continued to have an effect after the peak of metamorphism was reached in the South West Highlands.
4.5.2 Metamorphism:

The secondary metamorphism occurred in at least two stages, associated with two stages in the textural evolution of the assemblages. The first, and more complex, stage was the growth of albite porphyroblasts and the recrystallisation of the matrix mica fabrics; while the second stage concerns the growth of chlorite and K-feldspar, as a replacement of biotite and garnet. The earlier stages are therefore best developed in the high-modal-chlorite- pelites, found in Northern Kintyre, while the later stages are seen only in the k-feldspar-bearing pelites in South Bay. Due to the great lithological diversity of the protoliths in the areas affected by secondary metamorphism, several different types of assemblage were developed the minerals in each of these depending critically on the bulk rock composition.

Some of the rocks in the area, in the Beinn Bheula Schists, are highly oxidised. This has resulted in the production of spessartine-rich garnet, and the suppression of the growth of biotite. As a result, garnet in these rocks has remained stable throughout the secondary metamorphism, while biotite has not. Other assemblages, the Green Beds, have preferentially grown biotite in favour of chlorite, due probably to the low Al/Si ratios in the bulk rock chemistry. As a result of the disruption to the "normal" Barrovian mineral sequence, the rocks which experienced temperatures equivalent to those of the garnet isograd in North Knapdale may be difficult to find in Northern Kintyre, since almandine-grossular garnet will not be stable under the fO2 conditions concerned.

Other secondary assemblages preserve remnants of the primary Barrovian assemblages. Almandine-grossular garnets are found as pristine inclusions in albite porphyroblasts, which grew during the early stages of the secondary metamorphism, while sphene is pseudomorphed and replaced by rutile and carbonate. This suggests that the rocks were warm enough to keep garnet stable during albite porphyroblast growth.

The chemistry of the phengites in these assemblages is correlated with the other phases with which they co-exist. The influences that result are similar to those inferred for the primary assemblages, with garnet and biotite-bearing assemblages having Si-richer phengites than chlorite-bearing biotite/garnet-absent assemblages. However, the growth of chlorite and k-feldspar at the expense of
biotite leads to Al richer phengite. Generally, higher "grade" mineralogy will be favored by Si-rich bulk rock chemistries, even when these are Mg-rich.

The earlier stages in the secondary metamorphism occurred while the rocks were at high enough temperatures to keep almandine-grossular garnet stable. Only the later stages in the secondary metamorphism, can be called truly retrogressive, in the sense that retrogression represents the replacement of higher-temperature-stable by lower-temperature-stable assemblages.

The major implication of this chapter, as far as the thermal history of the South West Highlands is concerned, is therefore that the deeper levels of the crust remained at high temperatures for long enough after the primary deformation to allow a set of overprinting assemblages to grow in the presence of a deformation whose style was distinct to that of the primary deformation. The implication is that, if there was a significant time gap between the primary metamorphism and the earlier stages of the secondary metamorphism, the cooling rates in the South West Highlands were relatively slow. This is therefore further evidence that the thermal history in the South West Highlands was distinct to that in other parts of the Scottish Dalradian. Subsequent chapters will address these contrasts more fully.
CHAPTER 5
THE PRESSURE-TEMPERATURE CONDITIONS OF METAMORPHISM

"I can be quite obscure, and sometimes practically marzipan..."

-Mervyn Peake

In an integrated study of regional metamorphism, quantitative estimates of the P-T conditions of metamorphism are needed, especially if the aims of the study include the construction of P-T-t histories. In such a study, the changing P-T conditions with time need to be quantified. This chapter is intended to make estimates of P-T conditions of metamorphism in primary and secondary assemblages, thus characterising the P-T-(relative time) histories of the South West Highlands. The next chapter, on geochronological studies, will put absolute time constraints on the relative time histories produced here. The P-T estimates will therefore help to constrain speculations on the thermal structure of the crust in the South West Highlands during regional metamorphism made in sections 3.5 and 3.6.

The models of England and Richardson (1977) showed that the P-T conditions preserved in metamorphic assemblages are loci on independent P-T-t paths, and do not represent any geothermal gradient present in the crust during regional metamorphism. The array of P-T conditions preserved in a metamorphic belt is called the piezothermic array, and the P-T conditions occupied by the piezothermic array dictate the facies series of the metamorphic belt, in the sense of Miyashiro (1961). England and Richardson (1977) showed that "Barrovian" facies series P-T conditions are obtained with average rates of crustal heat production and conductivities, and it has become clear in subsequent studies that departures from Barrovian facies series regional metamorphism require differing tectonic settings (eg, isothermal uplift in granulite terrains (Bohlen 1987), rifting for Buchan terrains (Wickham and Oxburgh 1987), rapid uplift or under-thrusting of cool crust in blueschist terrains (Draper and Bone 1981)). Thus, as argued by England and Thompson (1984), precise knowledge of the P-T conditions and their variation with time is vital in the elucidation of the fundamental controls of regional metamorphism.
The pressure estimates will be made using thermodynamic calibrations of some of the reactions that occurred, and that have been described in detail in previous chapters, and the mineral equilibria that resulted during metamorphism of primary and secondary pelitic assemblages. Both primary and secondary assemblages show evidence of chemical and textural disequilibrium, with trends of changing mineral chemistry accompanying their textural evolution (chapter 4). As a result, semi-quantitative phase relations of low to medium grade pelites will be derived, so that the chemical changes can be related to changing P-T conditions. The effects of chemical dis-equilibrium can therefore be accounted for when interpreting the pressure estimates that will be made.

Temperature estimates will be made using mainly Fe-Mg exchange geothermometers. For one of the geothermometers to be used, the garnet-biotite Fe-Mg exchange geothermometer, there are a number of different calibrations. In an attempt to introduce objectivity into a field in which it is very easy to be subjective, some of the calibrations of this geothermometer that are commonly used will be reviewed critically.

5.1 Semi-Quantitative Phase Relationships of Reactions in Pelitic Assemblages:

In sections 3.2 and 4.4, it was shown that the chemistry of phengite is a sensitive indicator of changing P-T conditions, and that phengite chemistry is correlated with the assemblage with which it co-exists, this assemblage in turn being controlled by the bulk rock chemistry. Phengites in equilibrium with chlorite only are more Al-rich than those in equilibrium with chlorite and biotite, at given metamorphic conditions. In addition, Massonne and Schreyer (1987) pointed out that phengite in equilibrium with k-feldspar and biotite will be more Si-rich than phengite in k-feldspar-absent assemblages. The phengite composition diagram of J.B. Thompson also indicates dependence of phengite chemistry on the co-existing assemblage, and has been shown to be consistent with observations made in this study. The relationships between phengite chemistry and mineral assemblage will be explored further in this section, and qualitative phase topologies for low to medium grade Barrovian pelites will result, the topologies being constrained by the available experimental data to be discussed in subsequent sections of this chapter.
Because there are problems and inconsistencies in the existing thermodynamic data for low to medium grade pelitic assemblages (5.3.1), the phase topologies derived here are simple, first order, and qualitative. The approach used is based on that of A.B. Thompson (1976), but P-T-X-TS phase relations will be investigated as well as P-T-X-FM relations (where X-TS and X-FM are the progresses of the Tschermarks' and Fe-Mg exchange reactions respectively, see also sections 3.2 and 4.4). Pattison (1987) studied P-T-X-TS and P-T-X-FM phase equilibria in the Ballachulish low-pressure contact aureole, demonstrating the strong dependence of mineral chemistry and mineral assemblage on bulk rock composition. A similar demonstration will be made here, and will be shown to be consistent with the conclusions drawn in sections 3.2 and 4.4.

5.1.1 Derivation of the P-T-X-TS and P-T-X-FM Phase Topologies in the KFMASH System:

The assemblage musc + bi + chl + ksp + qz + fluid is univariant in the system K\textsubscript{2}O-MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-H\textsubscript{2}O (KMASH). The phases in this assemblage are related by the reaction:

\[3 \text{chl} + 8 \text{ksp} = 3 \text{musc} + 5 \text{bi} + 9 \text{qz} + 4 \text{H}_2\text{O}\] (1)

For each univariant reaction, there is a family of divariant assemblages, in which the phases may show compositional changes involving the Tschermarks' (TS) exchange \(((\text{Mg,Fe})_2\text{SiAl}_2)\). Reactions involving TS can therefore be written to express these compositional changes; these are pseudo-divariant reactions because TS is not a true phase, but an independent exchange component. In the case of low to medium-grade pelitic assemblages, reaction (1) has the following family of divariant equilibria, TS operating to various extents on the sheet silicate phases phengite, biotite and chlorite:

\[1 \text{chl} + 2 \text{ksp} + \text{TS} = 2 \text{bi} + 4 \text{qz} + 2 \text{H}_2\text{O} \quad [\text{musc}]\] (2)
\[6 \text{musc} + 5 \text{TS} = \text{chl} + 2 \text{qz} + 6 \text{ksp} + 2 \text{H}_2\text{O} \quad [\text{bi}]\] (3)
\[3 \text{musc} + 3 \text{TS} = \text{bi} + 3 \text{qz} + 2 \text{ksp} + 2 \text{H}_2\text{O} \quad [\text{chl}]\] (4)
\[12 \text{musc} + 2 \text{bi} + 9 \text{TS} = 3 \text{chl} + 14 \text{ksp} + 2 \text{H}_2\text{O} \quad [\text{qz}]\] (5)
\[3 \text{musc} + \text{chl} + 4 \text{TS} = 3 \text{bi} + 7 \text{qz} + 4 \text{H}_2\text{O} \quad [\text{ksp}]\] (6)
\[\text{chl} + 4 \text{ksp} = 3 \text{musc} + \text{bi} + \text{qz} + \text{TS} \quad [\text{H}_2\text{O}]\] (7)

The absent phase in each of these equations is given in square brackets.
In the presence of excess quartz and fluid, the reactions (2)-(7) are related by the Schreinemaker's bundle in Fig. 5.1. This bundle is semi-quantitatively aligned in P-T space by the thermodynamic and experimental calibrations of (6) and (7) by Powell and Evans (1983) and Massonne and Schreyer (1987). All other topologies are speculative. This bundle is similar to that presented by Bucher-Nurminen (1987), but not equivalent, since Bucher-Nurminen (1987) made the tacit assumption that TS only operates on phengite. This assumption meant that the two reactions [musc] and [chl] became a single, degenerate, equilibrium. Bucher-Nurminen's (1987) treatment therefore results in internal contradiction, allowing the absence of one of the phengite solid solution endmembers in a reaction in which TS operates only on phengite, and causes displacement of this reaction in P-T space. The treatment of the system used here follows that of Pattison (1987) and resolves this internal contradiction.

In the Schreinemaker's bundle in Fig. 5.1, excess qz and fluid appear on the high-temperature sides of all the reactions except [bi]. Since the qz-richer side of a reaction involving TS will also preferentially stabilise Al-richer solid solutions of phases in which TS occurs, in all the reactions listed except [bi], increasing temperatures lead to Al-richer phengite, biotite and chlorite. These relationships are illustrated on Fig. 5.2. The bold arrow shows how Al-richer compositions are stabilised with increasing temperature in all reactions except [bi], in which the opposite occurs, Al-richer compositions being stabilised with decreasing temperature.
Fig. 5.1 Schreinemakers' bundle, in the presence of excess SiO$_2$ and fluid, of the divariant equilibria intersecting at any given P-T point on the univariant curve of reaction (I):
5.1.2 Prediction of Mineral Chemistry Changes With Changing P-T-X Conditions:

In the discussion below, I assume that progress of the TS exchange is monitored dominantly by changing phengite composition. This is because
Fig. 5.2 Displacement of the Schreinemakers' bundle in Fig. 5.1 along the univariant curve of reaction (1) with changing P-T.
Fig. 5.5 P-T-X-TS net from Fig. 5.2 with schematic isopleths of phengite chemistry in phengite co-existing with biotite and k-feldspar ([chl]) and with biotite and chlorite ([ksp]): at the point in P-T space marked "x", the chemistry of phengite in each of the assemblages is given by the isopleth passing through "x"; the isopleth for the [chl] assemblage is Si-richer than the isopleth for [ksp] assemblages.
biotite and chlorite act as a buffer of phengite chemistry, their variation with respect to TS is slight in comparison to that of phengite.

5.1.2.1 South West Highlands Assemblages:

Two univariant assemblages have been described so far in this thesis, the primary phengite-biotite-chlorite-bearing pelites (3.1.1, 3.2.2, 3.2.3) and the late secondary phengite-chlorite-k-feldspar-bearing pelites (4.3.1, 4.4.2). The reaction causing growth of the late k-feldspar+chlorite in pelites was the reaction (neglecting coefficients):

\[ \text{chl} + \text{ksp} = \text{pheng} + \text{bi} + \text{qz} + \text{fluid} \]

(see 4.3.1, 4.4.2).

This reaction is the biotite-isograd reaction of Mather (1970). Mather (1970) did not characterise the dependency of this reaction on bulk-rock Fe/Mg ratios, but did show that it occurs first in rocks with high Si/Al ratios. Fig. 5.2 shows how all reactions, excepting [bi], are displaced to lower temperatures in Si-richer compositions. Fig. 5.2 is therefore consistent with Mather (1970). Assemblages in which this reaction has gone to completion will be governed by [phl] and will have increased Al contents in phengites with lowering temperature. An example of such an assemblage is 71-3, which clearly has Al-richer
Fig. 5.4 AKF diagram showing how biotite is stabilised first in Si-rich assemblages, and co-exists with k-feldspar and Si-rich phengite in these assemblages (from Mather 1970):
phengite than the other, k-feldspar-absent secondary assemblages in apparent contradiction to the phengite composition diagram of J.B. Thompson (1979). The nets derived in this section actually show how this apparent contradiction can come about. Phengites in pheng-bi-chl assemblages become Si-richer as the temperature is lowered. The reaction (1) is crossed first in Al-rich assemblages, because the rocks are cooling, and therefore, Al-rich bulk rocks will stabilise pheng-chl-ksp assemblages before rocks whose bulk chemistry is Si-richer.

In section 3.2, the absence of biotite in Al-rich bulk rocks was demonstrated. The assemblages concerned were k-feldspar-absent primary assemblages and phengites in biotite-absent rocks were Al-richer than phengites in biotite-bearing rocks. These trends are also clearly compatible with the predicted trends with assemblages stable at higher temperatures growing first in Fe- and Si-richer rocks.

5.1.2.2 Implications for P-T calibrations:

In 5.4, geobarometric calibrations are applied to some of the South West Highlands pelites. These calibrations are of [chl] and [ksp], and are either thermodynamic or based on hydrothermal syntheses at well characterised P-T conditions.

The authors of one of the calibrations of phengite chemistry in pheng-bi-ksp assemblages, Massonne and Schreyer (1987), point out that the phengite in equilibrium with phlogopite and k-feldspar is richer in Si than the phengite in any other assemblage in low to medium grade pelites. The pressure estimates resulting from application of their calibration to other assemblages will therefore be minimum pressures. This observation is illustrated on Fig. 5.5. A rock at the P-T conditions "X" can have either pheng-bi-chl- or pheng-bi-ksp-bearing assemblages depending on the bulk chemistry. The isopleths passing through "X" are schematic indications of phengite chemistry, their intersection with the trace of the invariant point giving the Al/Si ratios of the phengites concerned. It is clear that the isopleths for the pheng-bi-ksp assemblage are Si-richer than the isopleths for the pheng-bi-chl assemblage. Only at the trace of the invariant point on the
diagram will phengite chemistries from different assemblages coincide.

It is therefore clear from the foregoing that the influences on the chemistry of phengites depends ultimately on the bulk rock Fe/Mg and Al/Si ratios. These ratios decide what assemblages grow in a rock at a given P-T and the assemblages decide what the phengite chemistries are. The trends are simple and straightforward and have already been made apparent in previous chapters: Al- and Mg-rich bulk rock chemistries stabilise lower-temperature assemblages than Si- and Fe-rich bulk rock chemistries. The exception to this basic rule is the reaction involving biotite-absent, k-feldspar-bearing assemblages, whose behaviour is the opposite to the other assemblages considered; in these assemblages, Fe- and Si-rich phengites are stable at higher temperatures and become Mg- and Al-richer as temperature decreases.

5.2 Geothermometry; Reactions and Calibrations:

The methods used for quantitative estimates of P-T conditions of metamorphism, geothermometry and geobarometry, are the subject of critiques by Essene (1982) and Powell (1985). The basis of geothermobarometry is the re-arrangement of the equation for the energy consumed or liberated during a chemical reaction:

\[ \Delta G_0 = \Delta H + P \Delta V - T \Delta S \]

\[ = -RT \ln K \]

where \( \Delta G \) is the total, or Gibbs, energy change of the reaction, \( \Delta H \) is the enthalpy change, \( \Delta V \), the change in volume, \( \Delta S \), the change in entropy, \( R \) is the gas constant, and \( K \) is the equilibrium constant of the reaction. At equilibrium, \( \Delta G = 0 \).

Calibration of equation (1) for the reaction of interest means that the dependence of the phases taking part on P-T conditions can be derived, and that pressures or temperatures of equilibration can be worked out from suitable assemblages as a result. Equations of the form given by (1) can be calibrated, either by direct experiment, or by empirical comparison of assemblages with other assemblages whose P-T conditions are already well-characterised. All chemical
reactions have a slope in P-T space whose gradient governs whether the equilibrium constant depends dominantly on temperature or pressure. If the slope, given by \( \frac{dT}{dP} \), is small, the equilibrium constant depends mainly on temperature, and the equilibrium is referred to as a geothermometer. In the opposite case, the reaction is referred to as a geobarometer (Fig. 5.6).

Geothermometers can usually be classified under three headings: intracrystalline exchange, intercrystalline exchange and solvus geothermometry. Intracrystalline exchange occurs as a result of the temperature-dependent partitioning of cations between discrete crystallographic sites within a single phase. Because there is little change in the quantities of end-members involved during the reaction, the molar volume change is small, while entropy changes are often large. These reactions are therefore well suited to be geothermometers. They are, however, susceptible to exchange and re-equilibration during cooling from the temperatures of reaction, because the cation transport distances between crystallographic sites are small.

Intercrystalline exchange geothermometers are the most widely used, and are usually based on the exchange of Mg and Fe between two co-existing ferromagnesian phases. These kinds of geothermometers have the same advantages as intracrystalline exchange equilibria, but are less susceptible to retrograde re-setting, because the transport distances are several orders of magnitude greater.

Solvus geothermometry is based on the common property shown by minerals of limited solid solution between end-members at metamorphic temperatures. This is usually due to differing ionic radii in cations of similar charge, the degree of solid solution increasing at higher temperatures due to increased entropy in the crystal lattice making it more "adaptable" and more able to take up variation in cation sizes.

As was shown by A.B. Thompson (1976), the positions of many Barrovian isograd reactions in P-T space depend very strongly upon Fe/Mg ratios, hence upon the FM exchange. Other exchange reactions, such as the TS exchange (chapter 3), which involve coupled substitutions of cations of varying ionic radii can be expected to have a greater volume change and, as such, make a suitable basis for geobarometry. These reactions therefore often involve several phases and, being more complex, are often less well constrained. This is unfortunate,
Fig. 5.6 Contrasting clapeyron slopes: the position of each reaction in P-T space varies with mineral chemistry.
since, as shown by England and Richardson (1977), pressure differences between metamorphic belts can have profound implications for their tectonothermal histories.

Powell (1985) pointed out that assessing the calibration used, and the results that different calibrations give, in an objective way is difficult. Geothermobarometry rests on the assumptions that there has been no exchange between the minerals taking part in the equilibrium to be used after their growth and equilibration, unless there has been a degree of retrogressive metamorphism, evidence for which should be apparent in the textures of the rocks concerned. This assumption is testable to some extent by the presence or absence of compositional zoning in porphyroblasts, but may, if violated, give spurious answers which may go undetected. Powell (1985) cited the paradoxical situation whereby a good calibration that is sensitive to re-equilibration is rejected in favour of a bad calibration that is not so sensitive, but which gives a "reasonable" answer through fortuitous circumstances. If the reasonable-ness of answers from geothermobarometry is decided upon by geological criteria, there might seem little point in going through the exercise of geothermobarometry unless as a means of reinforcing prejudice. Calibrations should be accepted or rejected according to factors that are independent of the rocks studied, such as the quality of experimental data and procedures, if the calibration is experimental or thermodynamic, or how well characterised the rocks are, if the calibration is empirical.

Because Barrovian mineral assemblages are stable across a wide range of pressure conditions, first-order constraints on pressure variations are harder to obtain than similar constraints on temperature, because isograds are dominantly temperature-dependent. Thus "anomalous" pressures (such as will be calculated in this chapter) may be less credible as there will be little independent evidence for them in the mineral assemblages developed. Thus the emphasis in this chapter will be upon the characterisation of the pressures of metamorphism in primary and secondary assemblages as rigourously as possible. In addition, the chemographic changes and phase equilibria already described (sections 3.2, 4.4, and 5.1) will be related to changes and contrasts in P-T conditions more rigourously than before.

As has been detailed in previous chapters, the mineral assemblages developed during the primary metamorphism often bear ferromagnesian phases. In the
garnet zone, the pelites are sometimes garnet and biotite-bearing. Thus Fe-Mg exchange thermometry is potentially fruitful in these assemblages. In contrast, the biotite zone assemblages are more difficult, due to the absence of more than one thermodynamically well-constrained ferromagnesian phase. However, carbonate phases are widespread and occur in both metabasic and metasedimentary assemblages. Calibrations of three equilibria are applicable to the primary assemblages; the calcite-dolomite "solvus", the garnet-biotite, and the garnet-hornblende Fe-Mg exchanges. The first method is to be used in the biotite zone, while the second and third equilibria are to be used in the garnet zone. Most of the calculations of temperatures of metamorphism are based on analyses found in other studies, especially Graham (1974), Graham et al. (1983), and Greig (1985). Some new calibrations of the calcite-dolomite "solvus" and the garnet-biotite geothermometers have been made since these studies, so a re-appraisal is necessary and will be carried out here.

5.2.1 Calcite-Dolomite "Solvus" Geothermometry:

Harker and Tuttle (1955) suggested that temperatures of equilibration could be derived from the solvus between calcite and dolomite. This is one solvus of many found in the CaCO$_3$-MgCO$_3$-FeCO$_3$ system and has been investigated in a number of studies over the years. However, these have tended to treat each join in the Ca-Mg-Fe carbonate systems as binaries, and not as parts of a larger ternary system. Small amounts of a third component can affect the temperatures that result from the application of a calibration that assumes that this component is absent, or insignificant. In addition, it has been shown that differing experimental calibrations of the calcite-dolomite solvus can give mutually contradictory results. The most recent study of the Ca-Mg-Fe carbonate system is that of Anovitz and Essene (1987a) who derived the solvi in this system empirically from experimental reversals at known temperatures and from analyses of well-characterised natural systems and modelled these solvi thermodynamically. Their calibrations of the CaCO$_3$-MgCO$_3$-FeCO$_3$ system are given in table 5.1. These calibrations, and that of Powell et al. (1984) (Fig. 5.7) will be used in this chapter.
Fig. 5.7 Calibrations of calcite-dolomite geothermometry derived by Powell et al. (1984) and used in this chapter (from Powell et al. 1984)
5.2.2 Garnet-Biotite Fe-Mg Exchange Thermometry:

This equilibrium has probably received more attention than any other, because the assemblage concerned is particularly common and the phases are relatively well-constrained thermodynamically. In addition, the exchange between Fe$^{II}$ and Mg is one that might be expected to behave in a close-to-ideal manner, since the ionic radii and charge of the two cations are very similar. The Fe-Mg exchange reaction between biotite and garnet can be written as follows:

$$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH}_2) \rightarrow \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$$ (1)

The distribution coefficient, $K_d$ is given by:

$$K_d = \frac{(X_{\text{alm}})^3}{(X_{\text{gt}})^3} \cdot \frac{(X_{\text{phl}})^3}{(X_{\text{pyt}})^3} \cdot \frac{(X_{\text{ann}})^3}{(X_{\text{bl}})^3}$$

where $X_j$ is the mole fraction of endmember $j$ in phase $i$.

Despite being an apparently straightforward calibration, this equilibrium has several potential problems associated with it. Firstly, garnet often has high Ca and Mn contents. While Mn has a similar ionic radius and charge to Fe and Mg, the ionic radius of Ca is different, and its substitution for Fe and Mg therefore needs to be modelled as a non-ideal exchange. Biotite, in addition often has high octahedral Al and Ti contents. The high Al and Ti contents at present have not received much attention experimentally, but are likely to affect Fe/Mg ratios (e.g., Goldman and Albee 1977). Thus far, attempts to account for non-ideality in this equilibrium have centred on garnet, though the deviation from ideality of biotite may be significant. Secondly, the electron probe cannot distinguish between Fe$^{II}$ and Fe$^{III}$, and as was shown in chapter 4, the Fe$_2$O$_3$ content in biotite may be significant, but difficult to characterise without wet chemical analysis.

In high grade rocks, there is ample evidence for retrograde re-setting of the garnet-biotite exchange (e.g., Tracy 1982) and the geospeedometry equations of Lasaga (1983) show that the greatest alterations of Fe/Mg ratios as a result of
retrograde exchange by diffusion will occur on the rim of garnet, where analyses are usually taken. This, however, is not likely to be a problem in the rocks in the South West Highlands (section 3.3), though garnets at higher grades in the South West Highlands show limited evidence of exchange after their growth.

Three studies that have attempted to account for non-ideality in garnet and to model this thermodynamically are Hodges and Spear (1982), Ganguly and Saxena (1984) and Geiger et al. (1987). In addition, Goldman and Albee (1977) studied the effects of Al\textsubscript{i1} and Ti in biotite, and Ca and Mn in garnet, while Anovitz and Essene (1987b) investigated the almandine-grossular join. There will now follow a review of some of these studies, following which, calibrations of the garnet-biotite Fe-Mg exchange equilibrium will be derived.

Hodges and Spear (1982) used the presence of assemblages bearing one or more of all three AL\textsubscript{2}SiO\textsubscript{5} polymorphs within a small area of a metamorphic terrain to render a number of calibrations of equilibria consistent with the inferred P-T conditions of the Al\textsubscript{2}SiO\textsubscript{5} triple point of Holdaway (1969) (ca. 3.3 kbar, 501 °C). By assuming that Fe-Mg mixing in biotite was ideal, and urging caution in the case of assemblages with Ti-rich biotite, this study used a four-component mixing model to model the behaviour of garnet. This model assumed that all the joins in the garnet solid solution except the grossular-pyrope join were ideal. Ganguly and Kennedy (1974) inferred that the spessartine-pyrope join was strongly non-ideal, but Hodges and Spear (1982) found that temperatures close to 500 °C (similar to that of the Al-silicate triple point) were only derived if this join was modelled as being ideal.

Ganguly and Saxena (1984) produced a model for garnet end-member mixing by fitting of experimental and natural data from a number of sources, and suggested that, while the almandine-grossular join was close to being ideal, the almandine-pyrope join was not, but showed a strong deviation from ideality, especially at Fe-rich compositions - those which are most common in crustal metamorphic rocks. This is a major contrast to the model of Hodges and Spear (1982) and is the opposite of what might be expected given the far closer similarity between Fe and Mg than between Fe and Ca.

In their experimental study, Geiger et al. (1987) found further evidence for non-ideality in the almandine-pyrope join. This non-ideality was found to be stronger than that inferred by Ganguly and Saxena (1984) and was found to be
asymmetric. Using the data of Geiger et al. (1987), Anovitz and Essene (1987b) showed that a small degree of non-ideality in the almandine-grossular join was necessary to render some of the equilibria they were calibrating consistent with experimental reversals.

There is, however, substantial evidence that attempts to account for non-ideal behaviour in garnet lead to "less reasonable" results than the assumption that both biotite and garnet behave ideally. Ganguly and Saxena (1984) recognised that assuming garnet to be ideal gave a Gibbs energy of reaction change ($\Delta G_0$) for the Fe-Mg exchange between biotite and garnet that was more consistent with the available thermodynamic data than their model for non-ideal behaviour. These authors suggested that biotite behaving non-ideally, but in the opposite "sense" to garnet would explain this discrepancy within their model.

Chipera and Perkins (1988) applied a number of calibrations of the garnet-biotite geothermometer, assuming both ideality and non-ideality, to natural samples and showed that the calibrations assuming ideality were the most precise (ie, the most reproducible, and robust to compositional variations), while the calibration of Ganguly and Saxena (1984) was the least precise. The garnet analyses used by Chipera and Perkins were all low in Ca compared with typical Dalradian garnets (eg Dempster 1985a, Moles 1985, this thesis section 3.3). Thus, the dominant influence on the answer derived from a calibration assuming ideality was the Fe/Mg ratio of the two phases. In contrast, the results from the "non-ideal" calibrations were affected by the very corrections designed to make them robust against compositional variation and deviation in the two phases. If the results of Chipera and Perkins (1988) for the "ideal" calibrations were affected by, for example, high Ti in biotite, or high Ca and Mn in garnet, this would have been manifest in non-correlation between the $K_D$ values and the temperatures. The non-correlation was present in the application of the non-ideal calibrations.

These results are due therefore to one of two possibilities:

1. the Fe-Mg joins of both garnet and biotite behave ideally, and compositional variation between samples of these two phases does not affect their thermodynamics significantly. Thus the "ideal" calibrations will be applicable across a wide range of compositions.
2. The Fe-Mg joins of both garnet and biotite behave non-ideally, but fortuitously, the effects of this in both phases tend to cancel each other out so that the system displays behaviour that can be interpreted as being ideal.
Given that the "ideal" calibrations of the garnet-biotite geothermometer are based on direct fits to experimental data (Ferry and Spear 1978, Perchuk and Lavrent’eva 1983), the parameters that result from this fit will include in them any excess enthalpy of mixing that may be present due to non-ideality. As a result, there is nothing in the data used in these calibrations which indicates whether non-ideality is present or not, because the data consist simply of measured Kd values as a function of temperature. It is this function that is fitted to expressions relating thermodynamic parameters to temperature and pressure. These parameters will include excess energies due to non-ideality but the magnitude of these is unknowable from the experimental data, used for calibration, alone. Therefore, errors made by assuming that mixing is ideal will self-compensate, as long as this assumption is taken for both phases. If a correction is made for non-ideal mixing in only one of the two phases, inconsistencies may result. However, corrections must be made if Ca and Mn contents are high; the experimental data do not include these corrections, since they dealt with binary Fe-Mg solid solutions only. Calibrations for garnet-biotite geothermometry used in this study are listed on tables 5.2 and 5.3.

5.2.3 Garnet-Hornblende Fe-Mg Exchange Geothermometry:

The third equilibrium to be used as a geothermometer in this study is the Fe-Mg exchange reaction between garnet and hornblende. This reaction can be written as:

\[
\begin{align*}
\frac{1}{4}\text{NaCa}_2\text{Fe}_4\text{Al}_3\text{Si}_6\text{O}_{22}(\text{OH})_2 & + \frac{1}{3}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \\
\text{Fe-Pargasite} & \text{Pyrope} \\
= & \\
\frac{1}{4}\text{NaCa}_2\text{Mg}_4\text{Al}_3\text{Si}_6\text{O}_{22}(\text{OH})_2 & + \frac{1}{3}\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} \\
\text{Pargasite} & \text{Almandine}
\end{align*}
\]

for which the equilibrium constant is given by:

\[
K = \left(\frac{a_{\text{g}^t}}{a_{\text{py}^t}}\right)^{1/3} \cdot \left(\frac{a_{\text{hbl}}}{a_{\text{Fe-pa}^t}}\right)^{1/4}
\]

Unlike the garnet-biotite equilibrium, only two attempts have been made to
Table 5.1: Calibrations for calcite-dolomite solvus geothermometry:

Anovitz and Essene calibration for the binary Ca-Mg solvus:

$$T = A(x_{MgCO_3}^{CC}) + B/(x_{MgCO_3}^{CC})^2 + C(x_{MgCO_3}^{CC}) + D(x_{MgCO_3}^{CC})^{0.5} + E$$

Anovitz and Essene calibration for the ternary system:

$$T_{Fe-Mg} = T_{Mg} + a(x_{FeCO_3}^{CC}) + b(x_{FeCO_3}^{CC})^2$$

Coefficients for the Anovitz and Essene calibrations:

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-2360.0</td>
<td>a</td>
<td>1718.0</td>
</tr>
<tr>
<td>B</td>
<td>-0.01345</td>
<td>b</td>
<td>-10610.0</td>
</tr>
<tr>
<td>C</td>
<td>2620.0</td>
<td>c</td>
<td>22.49</td>
</tr>
<tr>
<td>D</td>
<td>2608.0</td>
<td>d</td>
<td>26260.0</td>
</tr>
<tr>
<td>E</td>
<td>334.0</td>
<td>e</td>
<td>1.33</td>
</tr>
<tr>
<td>f</td>
<td>0.32837</td>
<td>E 07</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Calcite-Dolomite Solvus Geothermometry; Temperature Estimates for Primary Biotite Zone Assemblages

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Powell et al. T (cc-dol)</th>
<th>Anovitz and Essene T (Mg-Fe cc)</th>
<th>$T_{Mg}$</th>
<th>$T_{Fe-Mg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8350</td>
<td>S.W. Jura</td>
<td>450-500</td>
<td>460-500</td>
<td>430-452</td>
<td>576-635</td>
</tr>
<tr>
<td>69-215</td>
<td>Tayvallich</td>
<td>415</td>
<td>420</td>
<td>339</td>
<td>420</td>
</tr>
<tr>
<td>69-212</td>
<td>Tayvallich</td>
<td>425</td>
<td>420</td>
<td>360</td>
<td>434</td>
</tr>
</tbody>
</table>

Calibrations are those of Powell et al. (1984) and Anovitz and Essene (1987). In the Powell et al. calibration, cc-dol is the Mg-calcite - Fe-dolomite, while Mg-Fe cc is the Mg-Fe calcite calibration. In the Anovitz and Essene calibration, $T_{Mg}$ treats Mg-calcite and Mg-dolomite as a binary, while $T_{Fe-Mg}$ allows for ternary mixing.
Table 5.3: Margules parameters for garnet solid solutions: (cal mol⁻¹)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Authors</th>
<th>G + S</th>
<th>A + E</th>
<th>H + S</th>
<th>G et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W^\text{Fe-Mg}$</td>
<td>200</td>
<td>-</td>
<td>0</td>
<td>1250 to 1550 (±150)</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Fe-Ca}$</td>
<td>4620 ±200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Fe-Mn}$</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Ca-Mg}$</td>
<td>4047±77</td>
<td>-</td>
<td>(3300 - 1.5 T)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Ca-Fe}$</td>
<td>0</td>
<td>165</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Ca-Mn}$</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$W^\text{Mg-Fe}$</td>
<td>2500 ±500</td>
<td>-</td>
<td>-</td>
<td>2416 to 2870 (±150)</td>
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</tr>
<tr>
<td>$W^\text{Mg-Ca}$</td>
<td>1000 ±77</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>$W^\text{Mg-Mn}$</td>
<td>3500</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Authors: G + S, Ganguly and Saxena (1984); A + E, Anovitz and Essene (1987b); H + S, Hodges and Spear (1982); G et al., Geiger et al. (1987)
Table 5.4: Garnet-Biotite Fe-Mg exchange calibrations: (T in kelvin, P in bars)

Ferry and Spear (1977):

\[ 0 = 12454 - 4.662T + 0.057P + RT \ln K \]

Hodges and Spear (1982):

As Ferry and Spear, but

\[ K = K_d + \left( y_{\text{alm}} / y_{\text{py}} \right)^3 \]

Ganguly and Saxena (1984):

\[ T = \frac{A + \left[ W_{\text{FeMg}} (X_{\text{alm}} - X_{\text{py}}) + W_{\text{Ca}} X_{\text{gr}} + W_{\text{Mn}} X_{\text{sp}} / R \right]}{(\ln K_d - (\Delta S^0 / R) - \ln(X_{\text{alm}} / X_{\text{phl}})} \]

\[ A = 2089 - (0.8 W_{\text{Fe-Mg}} / R) + 9.45 P \text{ (kbar)} \]

\[ W_{\text{Fe-Mg}} = 200 \left[ \frac{Mg/(Fe+Mg)}{gt} + \frac{Fe/(Fe+Mg)}{gt} \right] \]

\[ W_{\text{i}} = W_{\text{Mg-i}} - W_{\text{Fe-i}} \]

Recalibration based on Geiger et al. (1987) and Anovitz and Essene (1987b)

\[ RT \ln y_{\text{py}} = \left[ 1400(X_{\text{alm}})^2 \right] + \left[ (3300-1.5T)(X_{\text{gr}})^2 \right] \]

\[ + \left[ 1235 + (3300 - 1.5T)(X_{\text{alm}} X_{\text{gr}}) \right] + \left[ (3300-1.5T)(X_{\text{gr}} X_{\text{sp}}) \right] \]

\[ + \left[ 1400(X_{\text{alm}} X_{\text{sp}}) \right] \]

\[ RT \ln y_{\text{alm}} = \left[ 1400(X_{\text{py}})^2 \right] + \left[ (3300-1.5T)(X_{\text{gr}})^2 \right] \]

\[ + \left[ 1565 - (3300-1.5T)(X_{\text{py}} X_{\text{gr}}) \right] + \left[ (165)(X_{\text{gr}} X_{\text{sp}}) \right] + \left[ 1400(X_{\text{py}} X_{\text{sp}}) \right] \]
calibrate the garnet-hornblende exchange, by Wells (1979) and Graham and Powell (1984), both of which are empirical. Graham and Powell (1984) were able to show that the Wells (1979) calibration was flawed, in that some of the assemblages used by Wells show evidence of disequilibrium, so only the Graham and Powell (1984) study will be discussed.

Graham and Powell (1984) used assemblages with co-existing clinopyroxene, amphibole and garnet to calibrate reaction (2) by regression of Kd values with temperatures derived from the experimental calibration of the garnet-clinopyroxene Fe-Mg exchange of Ellis and Green (1979).

The calibration that results is:

\[ T = 2880 + 3280 \times \frac{X_{Al}^T}{\ln K_d + 2.426} \]

The assumption of ideality in the almandine-pyrope join in garnet has already been discussed at length and the strong evidence from experimental data for non-ideality in this join has been stressed. In the case of the garnet-hornblende thermometer, the assumption of ideal Fe-Mg exchange was made during the calibration, by assuming ideal behaviour in garnet and clinopyroxene. A parameter for non-ideality was derived by Graham and Powell to account for non-ideality in the grossular-pyrope join. Errors in making the assumption of Fe-Mg ideality for Fe-Mg mixing in garnet are therefore likely to be self-correcting in the calibration of Graham and Powell for the same reasons as given above for the garnet-biotite Fe-Mg exchange. If the thermometer gives consistent answers, similar antipathetic behaviour in hornblende to that suggested for biotite has to be invoked. At present, there is little evidence available for the ideality or otherwise for the Fe-pargasite-pargasite join, and no crystallographic reason why self correction of errors from clinopyroxene to hornblende can be invoked (M.D.Welch, 1988 pers. comm.). However, it is probable that the statistical nature of this calibration means that Graham and Powell's non-ideality parameter accounts not only for non-ideal Ca-(Mg,Fe) behaviour in garnet, but also, all the non-ideal behaviour in reaction (2) as a whole.

Graham and Powell (1984) tested their calibration on a variety of assemblages whose grade of metamorphism was constrained well by reference to petrogenetic grids in the majority of cases. Good agreement with the estimated temperatures
resulted. However, Graham and Powell (1984) urged caution in the application of their calibration in that it is best suited to assemblages with low $f_\text{O}_2$, estimated peak temperatures of less than 850 °C and with garnets of Mn contents less than 10%. All these requirements are fulfilled by the rocks to which this calibration will be applied.

5.3 Application of the Geothermometry Calibrations:

The calibrations of the geothermometers discussed above will now be applied to some of the assemblages in the South West Highlands. Three specimens in the biotite zone were used for calcite-dolomite thermometry, while five garnet zone samples were used for garnet-biotite thermometry and four samples for garnet-hornblende thermometry (Fig. 5.8). The application of each of the calibrations to the assemblages in the South West Highlands will be discussed in turn.

5.3.1 Calcite-Dolomite Solvus Geothermometry:

The calibrations of Anovitz and Essene (1987a) and Powell et al. (1984) have been applied to two samples from the Tayvallich Peninsula (69-212 and 69-215), and one sample from Central Jura (8350) (Fig. 5.8). As was shown in chapter 3 from the assemblage and isograd distributions, the lowest grades of metamorphism in the South West Highlands were near Tayvallich, while grade increased both to the north-west and to the south-east. The presence of biotite in $D_1$-$D_2$ shear fabrics in the west of Islay indicates that metamorphism was of biotite grade at least as far north-west as the west of Islay. Thus, the temperatures in 8350 are expected to be higher than in the other two assemblages.

Given that the calcite-dolomite geothermometer is an intercrystalline exchange equilibrium, and the fact that calcite is reactive at low temperatures, exchange during cooling from the temperatures of equilibration of the assemblages can be expected. Therefore, several temperatures were calculated from each assemblage using the graphs of Powell et al (1984) and the highest values were taken as representing the closest compositions to those of the equilibrium assemblage. The compositions giving the highest temperatures were then used in the Anovitz and Essene (1987a) calibration and the results compared. On neither of these
Fig. 5.8 Location map of assemblages used for geothermometry.
calibrations is a pressure correction applied. According to Powell et al. (1984), the errors in not applying a pressure correction were insignificant, while the existing experimental data were not thought to be rigorous enough by Anovitz and Essene (1987a) to derive a pressure correction.

Results for 69-212 and 69-215 are shown on table 5.2. Because these assemblages were dolomite-bearing, the calibration of Powell et al. (1984) for co-existing calcite and dolomite was applied also, for comparison. In both assemblages, the highest temperatures are about 415 to 420 °C. In comparison, the Anovitz and Essene (1987a) calibration gave temperatures about 10°C higher.

In contrast to the relatively well-constrained behaviour of the two Tayvallich samples, sample 8350 shows more variability with some temperatures from the Powell et al. calibration being in excess of 550°C, although several results of between 450 and 500°C are present (table 5.2). The calcite in this specimen grows as inclusions in dolomite-ankerite porphyroblasts, and it was found that during electron probe analysis, de-focussing the beam increased the abundances of Mg and Fe in the analyses resulting in higher apparent temperatures. Applying the Anovitz and Essene calibration to these compositions gives temperatures in excess of 600°C.

The calcite-dolomite thermometry implies therefore that temperatures of primary metamorphism in the lowest grade areas were of the order of 430°C. Higher grade biotite zone temperatures are not well constrained by sample 8350, but may have been between 450 and 500°C. Additional evidence of temperatures of metamorphism to the north-west of Tayvallich is found in kyanite-bearing assemblages in Port Ellen, Southern Islay. Graham (unpubl.) has bracketted the breakdown of pyrophyllite to kyanite at temperatures of about 450°C, and this reaction will have been exceeded in the assemblages of Port Ellen.

5.3.2 Garnet-Biotite Geothermometry:

Calibrations of this equilibrium have been applied to five assemblages (Fig. 5.8). 77-101 is a pelite from near the garnet isograd, 71-4 and 84-22 are k-feldspar-bearing pelites with well preserved remnants of garnet and biotite from
South Bay near Tarbert, 71-43 is an amphibolite from the same locality, and 86-8 is a semi-pelite from Kennacraig, south-west of Tarbert. In all garnet-biotite geothermometry calibrations, pressures were taken to range between 6 and 10 kbar, the resulting temperatures varying usually by less than 25°C across this pressure range.

All the calibrations listed on table 5.4 were applied to 86-8, the chemical data and results being listed on table 5.5. The results vary very widely from below 200°C to over 700°C with the Hodges and Spear (1982) giving the most "sensible" results ranging between 525 and 550°C. In contrast, the Ferry and Spear (1978) calibration gives temperatures that are about 100°C lower and the Perchuk and Lavrent'eva (1983) calibration under-reads temperature disastrously, even when the grossular activities are calculated using the Ca correction of Hodges and Spear (1982).

The calibrations which include a specific correction for non-ideal mixing of almandine and pyrope in garnet also give a wide range in temperature with ca. 400°C from the Ganguly and Saxena (1984) calibration. Calculating the pyrope and almandine activities with a modification of the Hodges and Spear (1982) activity model accounting for the interaction parameters of Geiger et al. (1987) and Anovitz and Essene (1987b) gives the highest temperatures at ca. 700°C when using the Ferry and Spear (1978) calibration of pure Fe-Mg exchange. The Perchuk and Lavrent'eva (1983) calibration using this activity model gives temperatures of about 350°C.

The calibration that gives the results that are most consistent with the assemblage's being in the highest grade part of the garnet zone is that of Hodges and Spear (1982). The correction for Ca in this case leads to a reasonable, or consistent temperature estimate, but further corrections for Fe-Mg non-ideality produce less consistent results. These results are an illustration of the point made in 5.2.2 that correcting for Fe-Mg non-ideality in garnet alone, without making a similar correction for Fe-Mg non-ideality in biotite, will lead to inconsistency. In addition, the drastic inconsistency of the Perchuk and Lavrent'eva (1983) calibration may be due to the asymmetry of the Fe-Mg exchange in garnet, such that the Fe/Mg ratios in the garnets investigated by these authors were far removed from the Fe/Mg ratios studied here.

Though several different calibrations and combinations of corrections for non-
Analytical Data

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<th>Garnets</th>
<th>Biotites</th>
</tr>
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<tr>
<td></td>
<td>$X_{Fe}$</td>
<td>$X_{Mg}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>2</td>
<td>0.677</td>
<td>0.051</td>
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</tbody>
</table>

Temperatures (°C)

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<tr>
<th></th>
<th>F-S</th>
<th>P-L</th>
<th>H-S</th>
<th>G-S</th>
<th>F-S (B)</th>
<th>P-L (B)</th>
<th>P-L (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>440-470</td>
<td>170</td>
<td>520-550</td>
<td>390</td>
<td>715</td>
<td>445</td>
<td>200</td>
</tr>
</tbody>
</table>

ideality have been applied to 86-8, the fact that the Hodges and Spear (1982) calibration gives the most consistent results should not come as a surprise. Garnets throughout the Dalradian are rich in Ca, with mole fractions of grossular of about 25% being common. Thus, the compositions are far removed from the compositions studied by Ferry and Spear (1978) and this calibration should not be applied to assemblages with garnet chemistries such as are typically found in the Dalradian. The foregoing is therefore a cautionary tale; calibrations which appear to account for all possible non-ideality in garnets actually give highly inconsistent results, simply because non-ideality in biotite is entirely uncharacterised.

As a result of the foregoing, the Hodges and Spear (1982) calibration has been applied to the other assemblages. The results and chemical data used are listed in table 5.6. The assemblages from South Bay, give temperatures of between 475 and 515°C in the pelitic rocks while 71-43 gives less variable temperatures of 505 to 515°C. In comparison, 77-101 gives scattered temperatures of between 450 and 570°C. Using garnet analysis no. (2) of 77-101, which has the lowest Mn content gives 470 to 550°C, with an average of about 510°C. Thus, temperatures in this assemblage are close to, and often higher than, those in the South Bay pelitic rocks.

Since both 77-101 and the South Bay pelites show evidence of widespread retrogression, data from these assemblages must be treated with caution, but, given that the metamorphic grade has been shown to have increased from the garnet isograd to Tarbert, the temperatures from the South Bay pelites are low relative to the trend shown by 77-101 and 86-8. Evidence has been presented already for the South Bay rocks which suggests that they were still warm when the albite porphyroblasts grew, as garnet inclusions are still pristine, while other inclusion phases have been replaced (section 4.3). As a result, the garnet-biotite Fe-Mg exchange may have either remained open to, or re-opened at, the time of growth of albite porphyroblasts. The resulting temperatures might therefore be closer to those during albite porphyroblast growth than those of the primary metamorphism. Although 71-43 does not bear albite porphyroblasts, some of the biotite grew after the formation of the primary fabric, forming non-aligned porphyroblasts in between the planes of schistosity defined by the hornblende. The lower temperatures in 71-43 might also reflect active exchange after the "peak" of metamorphism.

The alternative is that the temperatures recorded in 86-8 do not represent the
Table 5.6: Analytical Data and Temperature Estimates from the Calibration of Hodges and Spear (1982):

**Samples 71-4 and 84-22:**

### Analytical Data

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<th>Sample</th>
<th>Garnets</th>
<th>Biotites</th>
</tr>
</thead>
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<td>$X_{Mg}$</td>
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<td></td>
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<td>0.649</td>
</tr>
<tr>
<td>84-22</td>
<td>3</td>
<td>0.655</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.694</td>
</tr>
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<td>0.686</td>
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Temperatures: (8 kbar < $P$ < 12 kbar)

<table>
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<th>Biotite no.</th>
<th>Temperature ($^\circ$C; Hodges and Spear 1982)</th>
</tr>
</thead>
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<td>71-4</td>
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</tr>
<tr>
<td>1</td>
<td>1</td>
<td>496 to 507</td>
</tr>
<tr>
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<td>2</td>
<td>502 to 513</td>
</tr>
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<td>84-22</td>
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</tr>
<tr>
<td>3</td>
<td>3</td>
<td>481 to 492</td>
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<td>6</td>
<td>486 to 497</td>
</tr>
<tr>
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<td>6</td>
<td>486 to 496</td>
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</table>

00 233
Samples 77-101 and 71-43:

Analytical Data

<table>
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<th>Sample</th>
<th>Garnets</th>
<th>Biotites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{Fe}$</td>
<td>$X_{Mg}$</td>
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<tr>
<td>77-101</td>
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<tr>
<td></td>
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<td>0.684</td>
</tr>
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<td></td>
</tr>
<tr>
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<td>4</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>71-43</td>
<td>1</td>
<td>0.640</td>
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<td>2</td>
<td>0.603</td>
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</table>

Temperatures: (8 kbar < $P$ < 12 kbar)

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<th>Garnet no.</th>
<th>Biotite no.</th>
<th>Temperature ($^\circ$C: Hodges and Spear 1982)</th>
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<tr>
<td>1</td>
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<td>471 to 483</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>501 to 513</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>447 to 457</td>
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<td>2</td>
<td>2</td>
<td>474 to 485</td>
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<td>3</td>
<td>523 to 534</td>
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<td>2</td>
<td>3</td>
<td>556 to 569</td>
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<tr>
<td>Sample 71-43</td>
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</tr>
<tr>
<td>1</td>
<td>1</td>
<td>506 to 517</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>504 to 515</td>
</tr>
</tbody>
</table>

00 234
temperatures at the time of primary metamorphism. The garnet zoning profile from this assemblage in Fig. 3.19 shows that post-growth exchange of Fe and Mg has occurred. If this exchange did occur, the high temperatures from 86-8 suggest that the crust in this region continued heating after the primary deformation. This alternative is favoured by the observation that the garnet zoning in 86-8 has been reset by post-growth diffusion, while the garnets in 71-4 and 84-22 show no such resetting (section 3.3). Continued heating after the growth of the primary assemblages is also consistent with the evidence from garnet zoning that the primary metamorphism took place while the garnet zone was being heated. Another implication of such exchange is that the crust must have remained at high temperatures for a long period of time, since the metamorphic grade of the assemblages concerned would not normally be high enough to cause diffusion of Fe and Mg in garnet. The possibility of such exchange raises the question of when both metamorphic temperatures and pressures were preserved. This question is addressed further in 5.4.3 in which estimates of cooling rates necessary to cause measurable resetting of zoning of Fe and Mg in garnet at the temperatures of the primary metamorphism are made.

The garnet-biotite Fe-Mg exchange thermometer indicates that temperatures in the garnet zone were about 500 to 530°C, possibly higher at higher grades, and suggest strongly, when taken with zone profiles from the highest grade assemblages studied, that the rocks remained at high temperatures for some time after the primary metamorphism, and that temperatures actually increased subsequently to the primary metamorphism, to about 550°C. Temperatures at the time of the growth of albite porphyroblasts at Tarbert can be estimated tentatively at ca. 450 to 500°C. Further information on the temperatures of the secondary metamorphism will be presented in section 5.3.

5.3.3 Garnet-Hornblende Geothermometry:

Because there is only one rigourous calibration of the Fe-Mg exchange between garnet and hornblende at the time of writing, the calculation of temperatures from this equilibrium will not need the same amount of discussion as the application of the garnet-biotite Fe-Mg exchange, except for the comparison of results from the two calibrations. Strictly, these two equilibria are not comparable directly as the calibrations that are applied were derived independently of one another, and do not form part of the same internally consistent data set. However, trends can be compared, and confidence in absolute
temperature values derived from both calibrations will be re-enforced if these are similar to one another.

Three assemblages have been analysed, and data from two more, published by Graham and Powell (1984) will be included in this discussion. Chemical data and results from the analysed samples are presented in table 5.7. Sample 84-1 is from South Knapdale, near to the coast of West Loch Tarbert, while 71-43, already discussed in 5.2.4.2, is from South Bay, and 69-101 is from Tigh an Droghinn, Central Knapdale (Fig. 5.7).

71-43 gives temperatures ranging between 500 and 525°C, in comparison with 500 to 515°C from garnet-biotite geothermometry in the same assemblage. In contrast, sample 84-1 gives temperatures ranging between ca 490 and 550°C, and 69-101 gives relatively high temperatures of 530 to 570°C. The analyses published by Graham and Powell (1984) give temperatures of between 530 and 540°C; the samples come from Central and Southern Knapdale. Thus, most of the data from the garnet-hornblende geothermometer are consistent with the data from the garnet-biotite geothermometer. The major anomaly is sample 69-101 which appears to over-read temperature substantially. While in the other samples, Mn-poor garnets tend to give higher temperatures, in this sample, the Mn-poorest garnet gives the lowest temperatures. The Mn content in the garnet in this assemblage is substantially higher than in the other samples, at $X_{sp} \approx 0.1$.

Graham and Powell (1984) did not include a correction for Mn in their calibration and suggested that its use should be restricted to garnets with low Mn content. Although the garnets in this assemblage just conform to the limits set by Graham and Powell (1984), the correlation between higher temperature and Mn content displayed by this assemblage is clear.

Notwithstanding the discussion above, the agreement of the calibrations with one another is encouraging, especially since the garnet-biotite calibration was chosen from a set of calibrations which often purported to be more "realistic". The results suggest that the garnet zone experienced temperatures of about 510°C at the garnet isograd and up to 550°C at the highest grades, though these temperatures may not represent the temperatures of the primary metamorphism. The precision and reproducibility of temperature estimates from a given assemblage is poor, giving errors on these estimates of about 50°C, similar to the statistical errors normally associated with thermometry, based on accuracies of 00 236
Table 5.7: Garnet-Hornblende Geothermometry: Temperature Estimates and Analytical Data for Samples 69-101, 84-1 and 71-43:

### Analytical Data

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<tr>
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<th>Hornblendes</th>
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</thead>
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<td>$X_{Mg}$</td>
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### Temperatures:

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0 0 237
### Sample 84-1

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### Sample 71-43

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<table>
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<td>7</td>
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<td>497</td>
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</table>
electron probe analyses etc. (eg Powell 1985, Hodges and Crowley 1985).

5.4 Pressure Conditions of the Primary Metamorphism:

Many of the equilibria used for estimation of pressures of metamorphism are reactions in the system CaO-MgO-FeO-Al₂O₃-SiO₂-H₂O-TiO₂ (CMFAST), often involving anorthite or aluminosilicate phases (eg Anovitz and Essene 1987b, Ghent and Stout 1981). Unfortunately, none of the assemblages in the South West Highlands is aluminosilicate-bearing, except for the assemblages in Port Ellen referred to in the previous section, and the plagioclase is invariably almost pure albite. The result is that reliable pressure estimates from CMFAST equilibria cannot be derived, due to the poor constraints on activity-composition relations in Na-rich plagioclase, and the relatively large errors on anorthite abundances. This is unfortunate because these equilibria are often well constrained by experiment and by internally consistent thermodynamic data.

However, the chemistry of phengite in equilibrium with biotite, chlorite and quartz has been shown to be pressure-sensitive due to the Tschermak’s (TS) exchange. As a result, the main source of pressure constraint in this study will be based upon the chemistry of phengites, which has been well characterised in previous chapters.

5.4.1 Geobarometry Calibrations Applicable to Low to Medium Grade Pelites:

The two equilibria that have been calibrated thermodynamically and are of interest in the assemblages present in the South West Highlands are:

\[
3\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2 = \text{K}_5\text{Mg}_2\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{KAlSi}_3\text{O}_8 + 3\text{SiO}_2 + 2\text{H}_2\text{O} \quad (1)
\]

Celadonite = Phlogopite + k-Feldspar + Quartz + Fluid

\[
3\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2 + \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 = \]

Celadonite + Clinochlore

\[
\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 3\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + \text{SiO}_2 + \text{H}_2\text{O} \quad (2)
\]

Muscovite + Phlogopite + Quartz + Fluid

00 239
Both of these equilibria have been calibrated thermodynamically, by Powell and Evans (1983) and by Bucher-Nurminen (1987). Both calibrations are based on experimental data of Velde (1965), for Powell and Evans (1983), and Massonne and Schreyer (1987) for Bucher-Nurminen (1987).

Most of Velde's (1965) experiments were syntheses of phengites in equilibrium with k-feldspar, phlogopite and quartz, although two reversals were completed. Because Velde's (1965) experiments were only carried out over a limited pressure range, Massone and Schreyer (1987) carried out a comprehensive series of syntheses over the complete stability range of the assemblage phengite + phlogopite + k-feldspar + quartz as bracketed by Massonne and Schreyer, though none of the experiments were reversals. Both these sets of data were calibrated by their respective authors as thermobarometers of phengite chemistry, strictly only applicable to phengites co-existing with biotite, k-feldspar and quartz. As the run products, besides phengite, were not characterised chemically, the calibrations were presented as isopleths of phengite composition, of the number of Si atoms per formula unit (Si p.f.u).

These calibrations are effectively the stability limits of reactions of the form given by (1) above, but whose stoichiometry will vary according to the chemistries of the phases taking part. Using thermodynamic data, Massonne and Schreyer (1987) calculated the P-T location of the balanced reaction corresponding to the Si = 3.30 p.f.u. isopleth, and found that its position did not differ significantly from that of the isopleth. In addition, the starting materials used did not affect the compositions of the run products significantly. Thus, non-reversal did not appear to cause significant error. As was illustrated in section 5.1, application of each of these empirical calibrations to k-feldspar-absent assemblages results in minimum pressure estimates, because the [chl] equilibrium has the shallowest clapeyron slope (Figs 5.1 and 5.2).

Of the two experimental calibrations of phengite chemistry, I believe that of Massonne and Schreyer (1987) to be the more rigourous for the following reasons:

1. Velde's experiments were carried out over a relatively limited pressure range, resulting in most of the isopleths drawn by Velde above 4.5 Kbar
being positioned by extrapolation beyond the experimental constraints. In contrast, Massonne and Schreyer (1987) investigated phengite compositions at pressures up to 20kbar.

2. Velde assumed that the octahedral site occupancy in phengite ($\Sigma_{vi}$) was close to 2.00, and that variations from this were not significant. However, Massonne and Schreyer (1987) showed that the phengite whose Si p.f.u. was 3.30 had an $\Sigma_{vi}$ of 2.06. The equivalent phengite of dioctahedral site occupancy of 2.00 would have Si p.f.u. of 3.20. As a result, the phengite of a given Si content would record a significantly higher pressure in the Massonne and Schreyer calibration than in the Velde calibration. The phase relations concerned are illustrated in Fig. 5.9. Here, it is clear how Si p.f.u. increases with $E_{vi}$. It is also clear that phengite of $\Sigma_{vi} = 2.00$ could not co-exist with phlogopite and k-feldspar at all.

As a result, Velde's (1965) results may have been similar to those of Massonne and Schreyer (1987), but, by not recognising the significance of $\Sigma_{vi}$ greater than 2.00, Velde's resultant calibration would have under-read pressure significantly. Massonne and Schreyer (1987) point out that some of Velde's data are in fact consistent with the phase relationships in Fig. 5.9 and suggest that Velde's data are compatible with their own.

The thermodynamic calibration of Powell and Evans used the two reversed brackets in Velde's (1965) data to extract thermodynamic data for celadonite. Using this data, and data for the other phases taking part in reaction (1) from Powell (1978), calibrations for reactions (1) and (2) resulted (Fig. 5.10). These calibration assumes that the muscovite-celadonite solid solution was binary, therefore that $\Sigma_{vi} = 2.00$, as assumed by Velde.

In contrast, the calibration of equation (1) by Bucher-Nurminen (1987) was a statistical fit of fifteen synthesis data of Massonne and Schreyer (1987). Thus, no attempt at evaluating thermodynamic data for each of the phases involved was made, the parameters resulting from the statistical fit being values for the changes in entropy, enthalpy and volume of the reaction.

Bucher-Nurminen's (1987) calibration of reaction (2) avoids deriving thermodynamic data for celadonite, since reaction (2) is a linear combination of reaction (1) above, and the [TS] reaction in section 5.1:

$$2 \text{chl} + 8 \text{ksp} = 3 \text{musc} + 5 \text{phl} + 9 \text{qz} + 4 \text{fluid}$$
(3)
Fig. 5.9 Phase relations of k-feldspar-biotite-phengite assemblages in which $\Sigma vi$ in phengite is greater than 2.00: increasing $\Sigma vi$ leads to increasing Si pfu, and phengite with $\Sigma vi = 2.00$ cannot co-exist with both biotite and k-feldspar (from Massonne and Schrever 1987).

Fig. 5.10 Isopleths of thermodynamic calibrations of Powell and Evans (1983) for (a) phengite co-existing with chlorite and biotite, (b) phengites co-existing with biotite and k-feldspar (from Powell and Evans 1983):
Thus, by combining thermodynamic data for the phases in reaction (3) with the values for the molar volume, entropy and enthalpy changes found for reaction (1), a calibration of reaction (2) resulted. Both calibrations of Bucher-Nurminen (1987) are shown on Fig. 5.1.

Of these two calibrations, that of Bucher-Nurminen would normally be the more rigorous, as it depends on more experimental data, and on better experiment. In addition, the isopleths of the two Powell and Evans (1983) calibrations suggest that end member celadonite is stable at lower pressures than is indicated by Massonne and Schreyer’s (1987) experiments. In addition, the clapeyron slopes of each of Powell and Evans’ calibrations are very similar to one another, although Schreinemakers’ analysis of the set of reactions indicates that reaction (2) should have a steeper slope than reaction (1) (section 5.1). These are the principle reasons cited by Bucher-Nurminen for his recalibration.

The Powell and Evans (1983) calibration was based on the assumption that Σvi = 2.00. As shown above, this assumption results in significant under-reading of pressure in Velde’s empirical calibration of his own experiments. However, the phengite with Si p.f.u. = 4.00 would not be pure endmember celadonite because its Σvi would be greater than 2.00. Instead it would be a dioctahedral mica with a high celadonite activity and with a small but significant degree of solid solution towards trioctahedral mica (eg Monier and Robert 1986). The activity formulations used by Powell and Evans (1983) are to find the activity of pure celadonite in the phengite composition of interest, and the thermodynamic data derived are also for pure celadonite. Pure celadonite has not been synthesised by either of the authors reviewed here, and has not been shown to be stable. The errors in the assumption made by Powell and Evans (1983) therefore self-compensate in that the activity of pure celadonite endmember can be calculated in a natural phengite with significant solid solution towards trioctahedral mica.

In section 5.1, it was shown that reactions (1) and (2) intersect at the
Fig. 5.11 Isopleths of the calibrations of Bucher-Nurminen (1987) for the same reactions as calibrated by Powell and Evans (from Bucher-Nurminen 1987):

Fig. 5.12 Experimental reversals of the cymrite-celsian equilibrium: as shown by Moles (1985), the presence of this reaction gave good agreement in pressure estimates made with the phengite-biotite-chlorite geobarometer calibration of Powell and Evans (1983). Moles (1985) used brackets "a": a more recent series of experiments ("b") gives ca. 1 kbar higher pressures at 500°C resulting in better agreement of this reaction with the calibration of Powell and Evans (1983).
univariant reaction

\[
\text{chl} + \text{ksp} + \text{cel} = \text{musc} + \text{bi} + \text{qz} + \text{fluid} \quad (4)
\]

This reaction forms a stability limit for the assemblage investigated by Massonne and Schreyer (1987) and Velde (1965). In any thermodynamic calibration of reactions (1) and (2), the intersection of any pair of isopleths pertaining to a given phase composition should intersect along the curve in P-T space defined by experimental brackets of reaction (4). This reaction has been bracketed approximately by Massonne and Schreyer (1987) as passing through \( P = 3.5 \) kbar and \( T = 350^\circ \text{C} \), \( P = 7 \) kbar, \( T = 350^\circ \text{C} \) and \( P = 10.5 \) kbar, \( T = 400^\circ \text{C} \). However, as pointed out by Massonne (1987, pers. comm.), the \( \log K = 0 \) isopleths of Bucher-Nurminen’s calibration miss the correct intersection in P-T space by well over 100°C. The reasons for this are unclear, though they could lie in errors propagated by the rather roundabout method used by Bucher-Nurminen to calibrate reaction (2). The isopleths of Powell and Evans (1983) also "miss" the correct P-T location, though this is difficult to constrain accurately as the slopes of the two sets of isopleths are very similar.

The Powell and Evans (1983) calibration has been tested, both by these authors, and by Moles (1983, 1985) who compared it to the sphalerite geobarometer and the grossular-pyrope-anorthite-Al-silicate barometer of Ghent and Stout (1981). Good agreement resulted with these calibrations, though the Powell and Evans (1983) calibration tended to over-read in comparison with the other equilibria. In addition, the results of Moles (1985) were shown by him to be in good agreement with unpublished experimental brackets of a reaction between cymrite and celsian. As yet, the calibration of Bucher-Nurminen has not been tested to this extent. In the following part, both calibrations of reaction (2) will be applied to primary assemblages representative of the grades of metamorphism developed. The results will be compared to each other, and to those from the direct application of the empirical calibration of Massonne and Schreyer (1987).

5.4.2 Geobarometry:

Bearing in mind the problems associated with the geobarometers applicable to the South West Highlands assemblages discussed above, the two thermodynamic
calibrations of reaction (2) have been applied to 8 assemblages from Tayvallich, Knapdale and Northern Kintyre (Fig. 5.13). In addition, 3 assemblages from along-strike of Northern Kintyre, From Cowal and north-east Loch Fyne have also been assessed in this way. The phengite barometer of Massonne and Schreyer (1987) has also been applied to all of these assemblages, providing both a minimum pressure estimate, and a test of consistency of the thermodynamic calibrations of reaction (1).

The samples used for primary metamorphic pressure estimates are representative of all grades developed and of all structural levels exposed. 86-2 comes from Tayvallich, where the lowest grade rocks are exposed at the highest structural levels, while 86-8 represents the highest grades found, and 87-10 and 87-22 both represent the lowest structural levels. All of these assemblages, except 77-101 have uncrenulated, planar fabrics defined by phengite, biotite and chlorite, and show relatively little evidence of retrograde alteration of the primary mineralogy. For each thermodynamic calibration, two pressure estimates were made, one using the ideal site mixing model for the end-member activities recommended by Powell and Evans (1983), and the other assuming that $a_{\text{phl}} = \frac{\text{Mg}}{(\text{Fe} + \text{Mg})}$, as recommended by Bucher-Nurminen (1987).

Because phengite co-existing with biotite and k-feldspar is the richest in Si at given P-T conditions (section 5.1), application of the phengite composition barometer gives minimum pressure estimates. As a result, estimates from the phengite composition barometer of Massonne and Schreyer (1987) were made with the Si-richest phengite found in each assemblage. In contrast, the pressure estimates from the phengite-biotite-chlorite-quartz barometer were made with the average compositions of each phase. While the estimates were robust against the variations in chlorite, and phlogopite chemistry, these being relatively small, the variations in phengite chemistry result in pressure variations of ±1 kbar (Fig. 5.14). Powell and Evans (1983) and Powell (1985) show that the analytical errors associated with the phengite-biotite-chlorite-quartz barometer are ±0.5 - 1 kbar. Thus, reproducibility and accuracy are comparable.

The resulting pressure estimates are listed on table 5.8. The phengite composition barometer of Massonne and Schreyer (1987) yields estimates of between 7.5 and 10 kbar, with some assemblages from Kintyre and Cowal giving up to 11 kbar. These are minimum pressure estimates based on a rigorous, direct experimental calibration and therefore provide the standard to which estimates
Fig. 5.13 Location map of primary assemblages used for pressure estimates:
Table 5.8: Pressure Estimates for Primary Metamorphic Assemblages:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Pressure Estimates (kbar)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>P + E 1</td>
</tr>
<tr>
<td>86-2</td>
<td>Tayvallich</td>
<td>9-10</td>
</tr>
<tr>
<td>77-101</td>
<td>Garnet Isograd</td>
<td>11-12</td>
</tr>
<tr>
<td>86-10</td>
<td>North Knapdale</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>85-23</td>
<td>South Knapdale</td>
<td>11-12</td>
</tr>
<tr>
<td>86-8</td>
<td>Kennacraig</td>
<td>12-13</td>
</tr>
<tr>
<td>87-10</td>
<td>Northern Kintyre</td>
<td>11.5-12.5</td>
</tr>
<tr>
<td>87-22</td>
<td>Northern Kintyre</td>
<td>11.5-12.5</td>
</tr>
</tbody>
</table>

Cowal Assemblages:

| AR 1   | Ardentinny       | 13-14   | 4-5     | > > 20 | 4-5   | 12-13 |
| 86-50  | Loch Eck         | 11-12   | 4-5     | > 20   | 4-6   | 9-10  |
| 86-53  | Loch Fyne        | 11.5-12.5 | 5-6 | > 20 | 5-6 | 9-10 |

Calibrations and activity formulations used are:

P + E 1: Powell and Evans (1983), ideal site mixing models for all phases

P + E 2: Powell and Evans (1983), $a_{\text{phl}} = \frac{\text{Mg}}{\text{Fe} + \text{Mg}}$

B-N 1: Bucher-Nurminen (1987), ideal site mixing models for all phases

B-N 2: Bucher-Nurminen (1987), $a_{\text{phl}} = \frac{\text{Mg}}{\text{Fe} + \text{Mg}}$

M + S: Massonne and Schreyer (1987), the phengite composition barometer giving minimum pressure estimates
The only estimates from the phengite-biotite-chlorite-quartz equilibrium that are compatible with the phengite composition barometer are those from the Powell and Evans (1983) calibration using the ideal site mixing activity formulation for phlogopite. Estimates vary from 10 Kbar in 86-2 to 12 kbar in South Knapdale, Northern Kintyre and Cowal areas. Inclusions in albite porphyroblasts from South Bay give similar pressures. In all specimens, these estimates are higher than those from the phengite composition barometer.

Using $a_{\text{phi}} = \frac{Mg}{Fe+Mg}$ results in very low pressures of about 4 kbar for both calibrations, evidently incompatible with the phengite barometer estimates, while the site mixing activity formulation for the phlogopite end-member gives Kd values that are much higher than those which appear on Bucher-Nurminen’s isopleth diagram, log Kd values being invariably less than 1.0.

As a result, the thermodynamic calibration of Velde’s (1965) experimental data (Powell and Evans 1983) gives results that are compatible with the experiments of Massonne and Schreyer (1987), while the calibration of Massonne and Schreyer’s experiments (Bucher-Nurminen 1987) gives results that are manifestly incompatible, both with the experiments, and with basic petrogenetic grid considerations; this calibration implies that the rocks are either in the high pressure region of the eclogite facies, or are part of a Buchan facies series terrain. The results lend strength to the contention that the two sets of experimental results are in fact very similar to one another, as contended in 5.3.1, and suggested by Massonne and Schreyer (1987).

Sample 86-2 gives similar estimates of 10 kbar for both calibrations. This is probably because this specimen equilibrated closer to the location of reaction (4) in P-T space, bracketed by Massonne and Schreyer approximately at 10 kbar and 400°C. In contrast, two lower garnet zone samples, 77-101 and 86-10, give pressures from the phengite barometer that are low in comparison to other assemblages. While 77-101 has an appreciable secondary fabric, both samples have higher Al contents in their phengite than other specimens of similar grade. 86-10 does not have a secondary fabric, and Kd values from these samples for reaction (2) are similar to those in the other garnet zone assemblages.

If the values of these pressure estimates are to be taken at face value, they
show that the pressures of metamorphism increase, both with grade, and with
deepening structural level. The rocks in Northern Kintyre and Cowal seem to
have been about 6 km deeper at the time of primary metamorphism than the
rocks at Tayvallich (Fig. 5.13). This is more consistent with an initially inclined to
recumbent Tay Nappe during D$_1$-D$_2$ deformation (chapter 2) than with the
upright Tay Nappe precursor fold invoked by other studies of Dalradian structure
(eg Treagus 1987, cf Menclum and Fettes 1986).

It should be emphasised here that the models of England and Richardson
(1977) predict that (P-T)$_{S_{\text{max}}}$ conditions in a progressive metamorphic belt are
attained diachronously, and that pressures of metamorphism will increase with
increasing metamorphic grade. As shown by Dempster (1985), these predictions
are valid only if the uplift rates do not vary significantly across the region or
through time. As a result, the P-T conditions of metamorphism are consistent with
both of these predictions, since higher pressures are preserved at higher grades.
The subsequent chapters will deal with these points more fully, the timing of
metamorphism in the area being discussed in chapter 6, and the shapes of P-T-t
paths being discussed in chapter 7.

5.4.3 Geospeedometry; Post-(P-T)$_{S_{\text{max}}}$ Exchange and Re-equilibration:

In section 3.3, a complex garnet zone profile was described, and suggested as
being due to poly-phase garnet growth in the assemblage concerned, coupled with
some diffusion of Fe and Mn across the interface between core and overgrowth.
It was also suggested that this overgrowth occurred during the early stages of
secondary metamorphism, during D$_3$. If these suggestions are consistent, it is
probable that at least some of the P-T estimates made in this chapter do not
reflect the P-T conditions at the time of growth of the primary assemblages. Here,
these suggestions are tested and discussed by calculation of the cooling rates
necessary to cause noticeable diffusion of Fe at garnet zone temperatures (ca.
500-550 °C).

That two phases of garnet growth occurred in 86-8 cannot be disputed,
because of the abrupt discontinuities in the zoning profile (3.3.1). However, some
diffusion needs to be invoked to explain some of the features of this profile
implying in turn that the region cooled slowly. This is because diffusion is not
normally expected at garnet zone temperatures and "normal" regional
5.4.3.1 Methods; Cooling Rate Calculations:

The implication of the reset zoning is that the temperatures recorded by 86-8 will not be those of the primary metamorphism in this assemblage. In addition, it is possible that some post-growth exchange between phengites and other co-existing minerals may have occurred implying that the pressures recorded may also not be those of the primary metamorphism. These possibilities are to be assessed here, along with their potential implications for the preservation of P-T conditions of metamorphism in the assemblages likely to be affected.

Any process occurring in a cooling system, whose rate is strongly dependent on temperature, will slow down to a rate that is insignificant in the time-scales of observation over a relatively small temperature interval. This interval corresponds to the closure temperature of the process (see also Dodson 1973, 1979, Ganguly and Ruiz 1987, this thesis, section 6.1). The most common petrological application of the closure temperature concept is related to diffusion of species in solids. The species are usually elements that may be present in major or trace element quantities, and the solids are usually mineral grains though they may also be grain boundaries or fluids. In the case of diffusion, closure temperatures will depend on the rates of temperature change in the system, with rapid rates of temperature change leading to higher closure temperatures. In petrological systems, closure temperatures will also depend on the average distance a species needs to diffuse from its point of origin to a reservoir maintaining the equilibrium concentrations of the species concerned. This distance is referred to as the effective diffusion distance of the system; the concept of effective distance and its relation to grain size in a given rock is discussed in section 6.1 of this thesis.

Dodson (1973, 1979) gave expressions for the closure temperature in cooling systems, and these were used to estimate cooling rates. Calculations of closure temperature have been made for the interdiffusion of Fe and Mg in garnet using
the diffusion parameters of Cygan and Lasaga (1985), which are in good agreement with the parameters measured at higher temperatures by Elphick et al. (1985). The calculations used differing rates of cooling ranging between 1°C per Ma to 10°C per Ma, and effective diffusion distances of 0.1 mm and 1 mm. The cooling rates encompass all but the fastest cooling rates estimated by Dempster (1985) for the Dalradian of Perthshire and Angus, while the effective diffusion distances encompass the range between the length-scales of resetting by diffusion in 86-8 and the average grain size of the garnets seen in the South West Highlands. The results are shown in table 5.9.

5.4.3.2 Results; Closure Temperature Values and Cooling Rates:

The closure temperatures resulting from these calculations vary between 475 °C, for the slowest cooling rates and shortest effective diffusion distances, and 635°C for the fastest cooling rates and longest diffusion distances. The range in closure temperatures is large, and the dependency on cooling rate and diffusion distance strong, such that the calculated closure temperatures vary over a larger range than that of the measured temperatures in the primary assemblages. However, closure temperatures of 500 and 600°C for the shorter and longer effective diffusion distances respectively result from the cooling rate of 3°C per Ma. These closure temperature values bracket neatly the ca 550°C garnet-biotite temperature from 86-8.

If the rate of temperature change after the primary metamorphism was such that the closure temperature for Fe-Mg interdiffusion in garnet was less than 500 °C, measurable diffusion-resetting should be present in all the garnets analysed. However, if the closure temperature was more than 550°C, it is probable that no resetting would be noticeable in any of the garnets analysed. The abrupt onset of diffusion in garnets in natural prograde sequences with increasing grade and the closure temperature theory (section 6.1) both show that that diffusion rates become significant in heating and cooling systems over a short temperature interval. It seems that the "critical" temperature, whereby diffusion occurs such that its results are measurable, was exceeded by 86-8, during the over-growth of garnet, but not by the other, lower grade, assemblages, since the latter show few signs of diffusion in their zone profiles. Essentially, these calculations show that, if the rocks cooled at about 3°C Ma⁻¹ after the primary metamorphism, diffusion over 0.1 mm length-scales would have occurred.

Obviously, the calculations presented here are only first-order estimates of the cooling rates necessary to cause diffusion on measured length-scales. They do not necessarily imply that the South West Highlands cooled at about 3°C Ma⁻¹ after
Table 5.9: Results of closure temperature calculations for Fe-Mg interdiffusion in garnet using the expressions of Dodson (1979): parameters used are those of Cygan and Lasaga (1985).

<table>
<thead>
<tr>
<th>Cooling rate:</th>
<th>Effective diffusion distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 cm</td>
</tr>
<tr>
<td>1 °C Ma⁻¹</td>
<td>575</td>
</tr>
<tr>
<td>3 °C Ma⁻¹</td>
<td>600</td>
</tr>
<tr>
<td>10 °C Ma⁻¹</td>
<td>635</td>
</tr>
</tbody>
</table>

Temperatures given in °C, with an error of ±5 °C

Table 5.10: Temperature Estimates for Secondary Metamorphic Assemblages: these are approximate, due to the high bulk rock fO2 and the high Mn-contents in the garnets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(X-Mn)-gt (X-Fe)-gt</th>
<th>Garnet-Biotite</th>
<th>Garnet-Phengite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F-S</td>
<td>H-S</td>
<td>ideal</td>
</tr>
<tr>
<td>85-12</td>
<td>0.180</td>
<td>0.548</td>
<td>349-359</td>
</tr>
<tr>
<td>87-11</td>
<td>0.316</td>
<td>0.477</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.383</td>
<td>0.400</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.375</td>
<td>0.405</td>
<td>-</td>
</tr>
<tr>
<td>87-05</td>
<td>0.347</td>
<td>0.398</td>
<td>-</td>
</tr>
</tbody>
</table>

the growth of primary metamorphic garnet. What these calculations do imply, along with the presence of garnet over-growths with radically different chemistry to the over-grown cores, is that the South West Highlands remained at high temperatures for a long period after D1-D2 deformation. At cooling rates of 3°C Ma⁻¹, the region around Tarbert would have remained above 500°C, the approximate lower temperature stability limit of almandine-grossular garnet, for about 15 to 20 Ma after D1-D2 if primary metamorphism in this area occurred at 550°C. In comparison, cooling rates in the Perthshire Dalradian exceeded 20°C Ma⁻¹ (Dempster 1985) while cooling rates in the Alps and Himalaya were also greater than 20°C Ma⁻¹ (Hawkesworth et al. 1975, Zeitler et al. 1988, in press). Cooling rates in the South West Highlands were evidently anomalously low compared with other regional metamorphic belts.

5.4.3.3 Implications of Disequilibrium and Exchange for the P-T Estimates:

That the higher grade primary assemblages underwent a protracted mineral growth history is beyond dispute, as is the fact that this has resulted in dis-equilibrium. In this chapter, the phases used for geothermobarometry in pelites are phengite, chlorite, biotite and garnet. All these phases are interrelated by mineral equilibria (3.2), so it is likely that at least some of the P-T estimates made in this chapter are artifacts of this dis-equilibrium. The possibilities for this will now be discussed.

Of the South Bay assemblages analysed for thermometry, the pelitic rocks, 71-4 and 84-22, are texturally overprinted by k-feldspar-bearing secondary assemblages. The latest stages of this overprinting, involving the growth of k-feldspar and chlorite has not affected the garnet zoning (3.3.1), and biotite is often well-preserved in strain shadows (4.2.2). However, it is possible that, because pristine garnets are included in albite porphyroblasts, the earliest stages of the secondary metamorphism occurred within the garnet stability field. This might result in exchange of Fe and Mg between the garnet and the surroundings.

It is impossible to assess whether such exchange has occurred, and if so, whether it has affected garnet growth zoning significantly, due to the absence of garnet-bearing primary equilibrium assemblages at the same metamorphic grade. However, the relatively low temperature estimates from the South Bay rocks (5.3.2) may be explained by this exchange.

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86-8 also shows evidence in its texture of post-primary metamorphic activity, with slightly crenulated phengite and chloritisation of garnet and biotite. However, there is no porphyroblastic albite, but clastic albite is present. This assemblage has therefore undergone relatively little secondary metamorphism. The temperatures from this assemblage were suggested as being relatively high, at about 550°C. These higher temperatures will be those of the garnet over-growth phase, not of the primary metamorphism in this region. Hence, the area around Tarbert may in fact have continued heating after the primary metamorphism. This conclusion is consistent with the suggestion that the South Bay assemblages preserve evidence of exchange during cooling, simply because the South Bay rocks preserve the later stages of the secondary metamorphism, after the growth of albite porphyroblasts. The cooling-related exchange of Fe and Mg between garnet and the matrix postulated for the South Bay rocks would therefore have occurred during the early stages of the rocks’ P-T-t paths.

The effects of post-primary metamorphic exchange and dis-equilibrium on the pressure estimates is less easily constrained because garnet does not take part in the reactions used for barometry, though the growth of garnet at the expense of chlorite and phengite should have some effect on phengite chemistry (3.2.4, Miyashiro and Shido 1985). However, if the Tarbert area continued heating after the primary metamorphism, and was decompressing at the same time (see below, this section), one can predict that phengites buffered by biotite and chlorite should become Al-richer (section 5.1, Fig. 5.18). The thermal models presented in chapter 7 indicate that some heating of the crust at Tarbert did occur after primary metamorphism, and that this heating continued for up to 30 Ma afterwards.

Phengites from several garnet-zone pelites are shown in Fig. 5.19(a). 85-23 and 86-10 are two garnet-absent pelites with uncrenulated S₁-S₂ fabrics from Central-South Knapdale, while 77-101 is a highly crenulated micaceous pelite from near the garnet isograd in North Knapdale. The other assemblage shown is 86-8. The most petrographically overprinted assemblage is 77-101, which has the most variable phengite chemistry. The phengites in this assemblage are notably Al-rich (3.2.2, 3.2.3). The phengites in 86-8 also vary greatly, but are Si-richer than those in 77-101. In contrast, 85-23 and 86-10, which both have planar, uncrenulated farics, are also more chemically restricted. These assemblages therefore show strong correlation between the range in phengite chemistry, and the degree of petrographic and petrological over-printing and disequilibrium.
Phengites from several such assemblages are shown on Fig. 5.19a. 85-23, 86-10 are two quartz-phengite-biotite-chlorite-albite bearing assemblages from the garnet zone of Central Knapdale. The other assemblage shown is 86-8. The assemblage with the most signs of petrographic retrogression 86-8, which also has the greatest range in phengite chemistry. It was also noted in section 3.2 that the phengite 77-101 are distinctly Al-rich; this assemblage has a pervasively crenulated and recrystallised fabric. In contrast, 86-10 and 85-23 have smaller ranges in their phengite chemistries and show little or no signs of petrographic retrogression.

Fig. 5.19b shows phengite analyses from sample 87-22, which is from the North Kintyre coast to the south of Tarbert. The assemblage is a quartz-phengite-biotite-chlorite-albite bearing semipelite; the biotite is partly replaced by chlorite but the albite is clastic, not porphyroblastic. Hence, this assemblage is at a similar stage in its textural evolution to 86-8. The phengites in this assemblage are zoned, with the rims always more Al-rich than the cores, and therefore shows the Al-enrichment trend predicted above. The Al-enrichment in this assemblage is not due to the breakdown of biotite to chlorite; the correlation between phengite chemistry and assemblage described in 3.2.2 and 4.4.2 are due to Al-rich bulk rock compositions inhibiting the growth of biotite. The probable Al-enrichment trend is also shown by 77-101, which has a highly crenulated fabric and particularly Al-rich phengite for its position on the progressive sequence.

The conclusions concerning the scattering of phengite chemistry in these assemblages can therefore be summarised as follows:

1. Assemblages with textural evidence of overprinting metamorphism have a greater range in phengite chemistry than assemblages with little or no evidence of overprinting.
2. Many of the assemblages show evidence of Al-enrichment with time, whether this is from zoning (87-22), or from Al-rich chemistries associated with pervasive recrystallisation (77-101).
3. The highest grade assemblages show more scatter in their phengite chemistries than the lower grade assemblages; thus high temperatures for long periods of time can cause scatter and re-equilibration of phengites in the absence of deformation.

The implications of these observations for the pressure estimates made in this chapter are profound. Firstly, the suggestion that phengite became Al-richer after the primary metamorphism implies that the compositions closest to those at the time of the primary metamorphism were the Si-richest, hence that the high
pressures resulting from the assemblages CANNOT be explained as artifacts of the post-primary metamorphic re-equilibration. This is the most important implication for the pressure estimates that have been made in this chapter, and reinforces the confidence in their relatively high values.

Secondly, the zoning and scattering in the phengites shows that, as suggested by Massonne and Schreyer (1987), the kinetics of reactions involving phengites are sluggish, even when relatively high temperatures are maintained for long periods of time. This means that compositions reflecting varying stages in a rock’s P-T-t history may well be preserved, and that, if relatively few analyses are taken from the assemblage, the results may not reflect the full range in chemistry present. The chemical variations may be subtle, and undetected, especially if relatively little deformation or crenulation has occurred in the assemblage concerned.

Thirdly, the varying extents of disequilibrium and exchange present in the major element chemistries of the phengites analysed in this study imply that similar disequilibrium may also be present in the trace elements. The trace elements of most interest are Rb and Sr, for Rb-Sr geochronology. The possibility is that because Al/Si+Fe+Mg ratios may vary, and because phengites react sluggishlly, the separation techniques used (see appendices) may preferentially sample the Si-Fe-Mg-rich phengite, which may result in bias to older ages if the rocks were heating and decompressing, as is the case with the assemblages discussed here, or to younger ages, if the rocks were cooling along P-T-t trajectories shallower than isopleths of phengite chemistry (Fig. 5.18b).

Therefore, to conclude this section, the slow cooling postulated by Graham (1986) for the South West Highlands is supported by the reset garnet growth zoning found in the highest grade primary assemblage studied. In addition, the heating during primary metamorphism suggested by the garnet zoning (3.3.3) seems to have continued after the primary metamorphism. Thus, the primary metamorphism did not occur at the highest temperatures experienced by the rocks now preserved at the surface.

The reaction kinetics of phengites in the absence of deformation are slow enough to result in the preservation of various stages in the P-T-t history in many of the assemblages studied. This is in fact a good thing, because rapid kinetics would prevent the characterisation of the P-T conditions of the growth of the
phengites because reequilibration would be complete. However, caution, coupled with comprehensive coverage of the phengite chemistry, is needed, otherwise the picture emerging will be mis-leading. Similar caution is also needed for geochronology with phengites due to possible sampling bias. Thus, phengite ages in rocks collected from a polymetamorphic terrain should always be supported by a thorough characterisation of the chemistries of the phengites dated. The possible effects of sampling bias on the geochronological results of this study will be discussed further in chapter 6.

5.4.4 Consistency of the Pressure Estimates:

The major anomalous feature of the P-T estimates of the primary metamorphism is that the pressures are very high, the values of the pressure estimates being of a size normally associated with the blueschist facies. The preservation of high-pressure mineralogy on the regional scales seen in the South West Highlands has major implications for the thermal regime in force during regional metamorphism (chapter 7), so it is vital that the pressure estimates be tested as fully as possible, and that they be shown to be consistent. Although no other geobarometer is applicable to these assemblages, there are some ways in which the consistency of the pressure estimates can be tested. The first of these is a test of consistency with an experimentally calibrated reaction which has been applied to other assemblages, while the second test involves the peristernite solvus, and the third is an explanation as to why glaucophanic amphibole-bearing high pressure facies series mineralogy is not stabilised at the P-T conditions inferred for the primary metamorphism.

Moles (1985) noted that the Powell and Evans (1983) calibration tended to over-read pressure compared with the cymrile-celsian reaction-
\[ \text{BaAl}_2\text{Si}_2\text{O}_8\cdot\text{H}_2\text{O} = \text{BaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} \]

—and the other geobarometers applied by Moles, by about 1 kbar. However, a more recent unpublished calibration of this reaction indicates that it occurs at ca. 1 kbar higher pressures, at 500°C, than the calibration used by Moles (1985) (Fig.5.12). This implies that pressures were at least 10 kbar, as indicated by the phengite composition barometer.

In a detailed study of the peristernite solvus, which separates albite-rich plagioclase from oligoclase, Maruyama et al. (1982) recognised that it persists at
temperatures estimated to be up to 550 to 600° C in the high pressure (7-10 kbar) Sanbagawa Belt in Japan. Most of the plagioclase in the South West Highlands is very albite-rich, with the An component usually less than 1%. Only in Gigha, an island south-west of West Loch Tarbert, and along-strike of the higher grade part of the garnet zone, is An-rich plagioclase found, at 5 to 7% An (Graham 1974). As a result, the peritectite solvus has not been exceeded, except at higher grades of metamorphism (ca. 550° C). This observation is consistent with, but does not prove that, pressures were relatively high in the South West Highlands during the primary metamorphism.

Recalling that prograde metamorphism in the South West Highlands occurred early relative to the structural history of the Dalradian (chapters 2 and 3), evidence for early high pressure, low temperature metamorphic conditions of metamorphism is described by Gray and Yardley (1979) in the Dalradian of co. Mayo, Ireland. An exposure of crossite-epidote-haematite bearing mafic schist was found. This was a relict assemblage in a region dominated by Barrovian metamorphic assemblages. Thus, the high-pressure mineralogy in co. Mayo was a relict of assemblages that were presumably once more widely developed. The assemblage consisted of crossitic amphibole co-existing with epidote and haematite, with the crossite grains zoned to more glaucophane-rich compositions at their margins. These were overgrown by barroisitic and actinolitic amphibole, thus the blueschist facies mineralogy preserves an early stage in the evolution of the Dalradian metamorphic rocks in Ireland.

These assemblages are haematite-bearing, indicating high fO₂-metamorphic conditions. In contrast, all the mafic assemblages in Knapdale and Tayvallich are ilmenite-, or, rarely, magnetite-ilmenite-bearing, indicating a much lower fO₂ environment. As described in sections 4.3 and 4.4, high-fO₂ assemblages are limited to metasediments in the south-east of the study area. Crossite amphibole is often rich in Fe₂O₃ and Gray and Yardley point out that in high pressure greenschists (jadeite-bearing assemblages were not found), crossite-bearing assemblages are favoured by high fO₂ conditions. In contrast, the assemblages in the South West Highlands equilibrated under lower fO₂ conditions. Actinolite-hornblende bearing assemblages such as are found in the South West Highlands can therefore grow under high pressure metamorphic conditions. In the case described by Gray and Yardley, high-pressure low-temperature assemblages grew at an early stage in the metamorphic evolution of the area. The same has
happened on a regional scale in the South West Highlands. Evidence and reasons for this will be discussed further in subsequent chapters.

5.5 Pressure-Temperature Conditions of Secondary Metamorphism:

Equilibrium assemblages from the primary metamorphism are common, so the derivation of P-T conditions is relatively easy. In contrast, the characterisation of P-T conditions in secondary assemblages tends to be more difficult, since secondary assemblages tend to be over-printing and show much evidence of textural disequilibrium. As a result, the equilibrium compositions of the phases concerned are only obtained with difficulty. As a result, the P-T conditions of the secondary metamorphism are less well constrained than for the primary metamorphism, especially as the calibrations used involve fabric forming minerals.

Temperature estimates are based on calibrations of the Fe-Mg exchange between phengite and garnet; these would normally be well constrained since Fe/Mg ratios in phengites in the assemblages concerned do not show the same variability as Al/Si ratios. However, since the assemblages containing both these phases are highly oxidised, the garnets are very spessartine-rich, and the phengites may have high Fe$^{III}$ contents. As a result, the P-T conditions for the earlier stages in the secondary metamorphism are approximate, and not as rigorous as those for the primary metamorphism.

5.5.1 Temperature Conditions of the Secondary Metamorphism:

The Fe-Mg exchange reaction between phengite and garnet

\[
\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3\text{KFeAlSi}_4\text{O}_{10}(\text{OH})_2 = \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2
\]

Pyrope Fe-celadonite Almandine Mg-celadonite

for which

\[
K_d = \frac{(X_{\text{Mg-Mu}}X_{\text{Fe-Mu}})}{(X_{\text{Mg-gt}}X_{\text{Fe-gt}})}
\]
has been calibrated in three studies. Two of these are for eclogite facies assemblages and are not considered further. The third study (Hynes and Forest 1988) is a series of empirical calibrations based on the relationship between Kd values given by (2) and temperatures given by various calibrations of the Fe-Mg exchange between garnet and biotite. Although Hynes and Forest (1988) expressed a preference for a modified version of the Ganguly and Saxena (1984) garnet mixing model, based on what they believed to be more creditable temperatures for the rocks to which they applied the calibrations, their calibration based on the Hodges and Spear (1982) garnet mixing model is preferred here, for the same reasons as given for the garnet-biotite exchange in 5.2.2 above; the calibrations of garnet-phengite Fe-Mg exchange are empirical, so any effects of non-ideal Fe-Mg mixing in both phases are contained within the parameters of calibration. In addition, better fits to the data were found by Hynes and Forest (1988) for the calibrations assuming ideal Fe-Mg mixing.

The calibrations for ideal Fe-Mg mixing with no Ca correction and for the Hodges and Spear (1982) correction respectively are

\[
T(°K) = 4.09 \times 10^3 / (\ln Kd + 3.23) \quad (3)
\]

\[
T(°K) = 4.27 \times 10^3 / (\ln K + 3.35) \quad (4)
\]

where Kd is given by (2) and K is the equilibrium constant for (1), being Kd corrected according to Hodges and Spear (1982).

The temperature estimates resulting from these calibrations are necessarily approximate, because the phengites probably have high FeO contents. In addition, there is no correction for Mn in garnet. The calibrations are based on garnets with Mn contents ranging from 0.5 wt. % to 11 wt. %, and Hynes and Forest applied them to garnets ranging from 0.3 to 19 wt. % MnO. Apparently consistent results were obtained. As a result, the calibration appears to be robust against Mn variation. However, the effects of high FeO in phengite have not been tested but may be severe, though it is possible that the fO2 conditions in all the assemblages in the South West Highlands to which the calibrations were applied were similar, as the protoliths and the assemblages are very similar to one another (sections 4.3 and 4.4). If so, variations in Kd values should reflect variations in temperature.

Temperature estimates were made for three assemblages. 87-11 and 87-05 are...
assemblages with high modal chlorite from Northern Kintyre, while 85-12 is a garnet-biotite-chlorite-phengite bearing assemblage from North Knapdale, in which the garnet is spessartine-rich and grows in a crenulated fabric. Sample 85-12 did not necessarily equilibrate simultaneously with the high-modal-chlorite assemblages, but it is texturally close to equilibrium, and the presence of biotite allows comparison with garnet-biotite thermometry. The results are presented on table 5.10.

Firstly, garnet-biotite Fe-Mg exchange thermometry on 85-12 gives temperatures of 430 to 440°C, using Hodges and Spear (1982) and 349 to 359°C using Ferry and Spear (1978). In comparison, garnet-phengite thermometry gives more scatter, with estimates up to 20°C higher, using both (3) and (4) than the equivalent garnet-biotite calibration. Temperatures for garnet-phengite thermometry are therefore consistent with, but slightly higher and more scattered than, those for garnet-biotite thermometry.

Temperatures from 87-05 range between 453 and 493°C, using (4), while 87-11 gives higher values at 490 to 530°C, again using (4). Texturally, 87-11 preserves an earlier stage in the secondary metamorphism, with planar and uncrenulated fabrics and small albite porphyroblasts growing within these, than 87-05, which has a crenulated fabric folding and displacing larger albite porphyroblasts. Thus, 87-11 may therefore preserve higher approximate temperatures, based on the contrasting Kd values, as a result of its preserving an earlier stage in the textural evolution. This assumes that garnet and phengite continued to grow and equilibrate over a wide range of temperature conditions, which is consistent with the pristine nature of all the garnets present in the secondary assemblages.

These temperature estimates suggest that the earlier stages in the secondary metamorphism took place when the rocks were still relatively warm, possibly in excess of 500°C. This is consistent with the apparent stability of almandine-grossular garnet during the growth of albite porphyroblasts.

Chapter 3 showed that the highest grades of primary metamorphism preserved are seen at Tarbert, coinciding spatially with the onset of the pervasive secondary metamorphism. However, the rocks to the south-east of Tarbert may have increased further in grade, especially as one assemblage collected from Northern Kintyre with remnants of almandine-grossular garnet, 87-8, has higher Mg/Fe ratios than the garnet in 86-8 (section 3.3). Such an increase in grade would be
difficult to detect, because the rocks have undergone secondary metamorphism, and are highly oxidised, so tend not to preserve Barrovian assemblages.

Constraints on the temperatures of the later stages in the secondary metamorphism are derived from the growth of k-feldspar and chlorite at the expense of biotite. This was bracketted by Massonne and Schreyer (1987) approximately at 350 to 400°C, increasing with pressure. These brackets were in the Fe-free system, and the reaction concerned is displaced to lower temperatures with increasing Fe/Mg ratios (section 5.4). Thus, temperatures of the later stages in the secondary metamorphism are estimated to be about 300 to 350°C.

5.5.2 Pressure Conditions of Secondary Metamorphism:

The pressure conditions throughout the secondary metamorphism are derived on the assumption that biotite is in equilibrium with the rest of the assemblage, even though biotite is being broken down to chlorite (+ k-feldspar). The mineral compositions closest to equilibrium are also poorly constrained, so pressure estimates will be quoted using the full range of phengite compositions present in each assemblage. The calibrations and activity formulations used are those of Powell and Evans (1983) and Massonne and Schreyer (1987).

Three k-feldspar-bearing assemblages from South Bay were used for pressure estimates because these are the only rocks with significant modal biotite co-existing with chlorite. In addition, the mode of k-feldspar in the assemblages is low. Pressures were also calculated from 85-12, since this assemblage is texturally close to equilibrium. Because retrograde P-T-t paths are likely to be sub-parallel to phengite composition isopleths, the same Kd and Si pfu values are used to bracket the possible ranges in pressures for both the early and the late stages in the secondary metamorphism. The two stages are assigned approximate temperatures of 450 to 500°C and 300 to 350°C for the earlier and later stages respectively, based on section 5.5.1. The results are presented in table 5.11.

There are two fundamental problems associated with the pressure estimates from these assemblages (leaving aside those problems that may be associated with the calibrations used). Firstly, the assemblages are manifestly non-equilibrium assemblages; they preserve varying stages in the overprinting of primary assemblages, or of early secondary assemblages by later secondary assemblages.
Table 5.11: Pressure Estimates for Secondary Metamorphic Assemblages:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure Estimates (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P + E</td>
</tr>
<tr>
<td>84-22</td>
<td>6-8</td>
</tr>
<tr>
<td>71-4</td>
<td>6-7</td>
</tr>
<tr>
<td>85-12</td>
<td>-</td>
</tr>
<tr>
<td>71-1</td>
<td>6-8</td>
</tr>
</tbody>
</table>

Calibrations and activity formulations used are:

P + E: Powell and Evans (1983), ideal site mixing models for all phases

M + S: Massonne and Schreyer (1987), the phengite composition barometer giving minimum pressure estimates
Fig. 5.14 Reproducibility in pressure estimates from the calibration of Powell and Evans (1983) as a result of mineral chemical variation within each specimen:

Fig. 5.15 Suggested attitude of the Tay Nappe immediately after the primary metamorphism, and D₁-D₂ deformation, based on the P-T estimates made in this chapter, especially the increasing pressures in deeper structural level rocks: as suggested in chapter 3, the Tay Nappe at this time was inclined to recumbent.
Fig. 5.16 Pressure estimates from secondary metamorphic assemblages using the phengite-biotite-chlorite geobarometer of Powell and Evans (1983):
Calculating P-T conditions from an assemblage obviously requires that the assemblage preserve the mineral compositions of final equilibration, whereas it is likely that reaction between some of the phases in some of the assemblages has not gone to completion. The only justification offered for the pressure estimates are that retrograde P-T paths are likely, though not certain, to be sub-parallel to phengite composition isopleths (Fig. 5.18a). If this is the case, the errors resulting will be of the order of 1 kbar, and are therefore similar in size to the errors associated with the calibration (see also Powell 1985).

The other major problem with these pressure estimates is the fact that different assemblages preserve different stages in the rocks' P-T-t paths. The stage on the P-T-t path preserved is difficult to derive from the textures alone, since the progress of a given reaction in a given assemblage at given P-T conditions depends on bulk rock composition (see also section 5.1). It is therefore difficult to decide whether the differences in P-T estimates from overprinting assemblages are due to real differences in the parts of P-T-t paths preserved by the assemblage, or to imprecision in the geothermobarometry results, or to post-crystallisation exchange between the phases concerned.

However, the assemblages used here all preserve similar textural stages in the secondary metamorphism, being all k-feldspar-bearing pelites with phengite fabrics that are discontinuous with the inclusion trails in the albite porphyroblasts. These assemblages are therefore likely to have grown during the retrograde, or cooling, stage in the rocks' P-T-t histories, thus making it more likely that the parts of the P-T-t paths recorded in the assemblages are subparallel to phengite composition isopleths.

Though there is much scatter in the pressure estimates for both calibrations (Fig. 5.16), the reproducibility of the estimates between assemblages is reasonable. The Powell and Evans (1983) calibration gives pressures of 7 to 10 kbar at 450-500°C, and 4 to 7 kbar at 300-350°C. In comparison, the Massonne and Schreyer (1987) calibration, as expected, gives lower pressures of 4 to 7 kbar, and 3 to 6 kbar, at 450 to 500 and 300 to 350°C respectively.

The differences between the results of the two calibrations are presumably due to disequilibrium in the assemblages, and might be rationalised in a rather subjective and unscientific way by taking the Al-richer phengite (lower pressure) from Powell and Evans (1983), as the phengites in the k-feldspar-bearing
Fig. 5.17 The thermal structure of the crust (a) immediately before and (b) immediately after $D_1 - D_2$ folding, as postulated in chapter 3, and as confirmed by the $P-T$ estimates made in this chapter.
Two schematic P-T-t paths illustrating the effects of disequilibrium observed in garnet-biotite temperature estimates in (a) 86-8 (older phengites are Si-richer) and (b) the South Bay Secondary Pelites (sub-parallel paths mean that the effect on the pressure measurement is not large).

(b) Effect on pressure estimates from secondary assemblages of P-T-t paths non-parallel with phengite composition isopleths: unless the retrograde paths are relatively steep, or shallow, the effect on pressure estimates will not be large.
(a) Primary assemblages from the garnet zone: 86-8, the highest grade primary assemblage studied, shows more scatter in phengite chemistry than the other assemblages (85-23 and 86-10).

(b) Core-rim analyses from 87-22: the cores of given grains are consistently Si-richer than the rims, though analyses from different grains show considerable overlap.

Fig. 5.19 Sectors of A'KF diagrams showing detailed phengite chemistries of some of the primary assemblages described in chapter 3 and used for Rb-Sr age dating:
secondary assemblages become Al-richer with time, and comparing it to the Si-richest phengite (higher pressure) from Massonne and Schreyer (1987), as this calibration tends to under-read pressure. This would result in pressure estimates of 7 to 8 kbar for the earlier stages of the secondary metamorphism. Such a line of reasoning is best avoided if possible.

The alternative would be to accept that the Massonne and Schreyer calibration will not under-read pressure to the same extent at lower temperature, and to accept the resulting estimates in preference to those which were derived from mineral compositions that may not have been in equilibrium. The result from this line of reasoning is the same as before, with pressures estimated to be a minimum of 8 kbar for the earlier stages of secondary metamorphism, and about 6 kbar during the later stages. An additional problem is that temperatures of secondary metamorphism are not well constrained, because the assemblages may represent differing stages on the P-T-t paths in the area, and because of the oxidising conditions of metamorphism. It is unfortunate that better, more objectively sound, constraints cannot be gained, but the nature of the assemblages mitigates against this.

5.5.3 Conclusions:

Temperatures preserved in secondary metamorphic assemblages vary between 430 and 530°C from garnet-biotite and garnet-phengite Fe-Mg exchange theromometry. The temperature estimates are approximate, but the variation in them may be due to the varying stages of the secondary metamorphism preserved in these assemblages. They are consistent with the apparent stability of almandine-grossular garnet during the growth of albite porphyroblasts and the re-opening of the garnet-biotite and garnet-hornblende Fe-Mg exchanges. The temperatures at the time of albite porphyroblast growth may have been as high as 530°C which compares with the 470 to 520°C temperature estimates derived from the South Bay pelitic and mafic assemblages (5.2.1 and 5.2.2).

Although the garnets analysed are very rich in spessartine, the temperature estimates, if taken at face value, indicate that the metamorphic grade during the primary metamorphism may have continued to rise to the south-east of Tarbert, consistent with the deeper structural levels and higher metamorphic pressures of these rocks. Almandine-grossular garnet remnants in an assemblage collected
from Northern Kintyre have higher Mg/Fe ratios on their rims than the garnets from Tarbert (section 3.3) providing further evidence of such an increase in grade.

The temperatures of the later stages of the secondary metamorphism are constrained from the replacement of biotite with chlorite and k-feldspar to have been about 300 to $350^\circ$C.

Based on sparse and poorly constrained data, the pressures of secondary metamorphism were about 8 kbar at the earlier stages and 6 kbar at the later stages. These estimates are derived from assemblages in which k-feldspar had already started to grow, so pressures during the early stages of the secondary metamorphism would have been higher still. The implication here is that the amount and rate of regional uplift between the primary and the secondary metamorphic episodes were probably low, thus favouring slow cooling suggested by the relatively high temperature estimates itemised above. However, cooling and uplift between the early and late stages of the secondary metamorphism is very strongly indicated.

5.6 Conclusions and Implications:

The pressure-temperature conditions of both the primary and secondary episodes of metamorphism have been characterised as well as possible based on the specimens, assemblages and calibrations available. Though conclusions have been drawn already at the end of each of the sections of this chapter, they will stand re-stating so that they can be seen in context.

The lowest temperature estimates found in the biotite zone are from the Tayvallich area, where the highest structural levels and the lowest grade mineral assemblages are found. These temperatures are about 420 to $430^\circ$C, based on two rigorous and independent calibrations of calcite-dolomite solvus geothermometry. Higher temperature estimates are found to the north-west, on Islay, again consistent with higher grade mineral assemblages and associated with deeper structural levels. The temperatures are poorly constrained from calcite-dolomite geothermometry, and the presence of kyanite in phyllitic assemblages, to be between 450 and $500^\circ$C.

Temperatures in the garnet zone of Knapdale are constrained by garnet-biotite
and garnet-hornblende geothermometry to be between 510°C at the garnet isograd, and up to 550°C at Tarbert, again consistent with increasing grade and deeper exposed structural levels. Consistent temperatures from the garnet-biotite geothermometer were obtained only with the calibration of Hodges and Spear (1982). Good \textit{a priori} reasons for the acceptance of this calibration in favour of others are therefore supported by this consistency. The garnet zone rocks to the south-east of Tarbert are not constrained with respect to temperature during the primary metamorphism because they have been pervasively overprinted by the secondary assemblages.

Pressures of the primary metamorphism were probably at least 10kbar, based on minimum estimates from experimentally calibrated geobarometry. These estimates are backed up by similar and higher pressure estimates from thermodynamically calibrated geobarometers, but only if the calibrations and activity formulations of Powell and Evans (1983) are used. The pressure estimates tend to increase as deeper structural levels are exposed, consistent with an inclined to flat-lying nappe pile geometry as postulated in chapter 2. Taken with the increased temperatures in rocks from deeper structural levels, the pressure estimates indicate that the thermal structure of the thickened crust was like that postulated in chapter 3 (Fig. 5.16).

The higher grade primary assemblages show much evidence for elevated temperatures for long periods of time after the primary metamorphism, both in their textures and in their mineral chemistries. Relatively slow cooling rates of ca. 2 to 5°C per Ma are estimated from Fe-Mg coupled diffusion data in garnets, and the extent of resetting of growth zoning in garnets in the highest grade primary assemblage studied. The estimated cooling rate is simply an indication of the fact that the reset garnet zoning requires elevated temperatures for long periods of time, and is not to be taken as the rate of cooling after primary metamorphism, especially since the rocks may have continued heating after the growth of the primary assemblages.

The elevated temperatures recorded in the primary assemblages have resulted in increasing scatter in phengite chemistries at higher grades, indicating that the kinetics of reaction of phengite are slow, even in the presence of deformation. This scatter could have led to sampling bias and additional random error on the pressure estimates in these assemblages. However, these possible errors are unlikely to be able to explain the high pressures recorded in these rocks, since
phengites tend to become Al-rich over time.

The P-T conditions of the secondary metamorphic episode are not well constrained due partly to disequilibrium in the assemblages used and partly to extrapolation beyond the compositional ranges used in the calibrations. However, the estimates cover a wide range in P-T conditions, which may reflect the reasons for poor constraint just itemised, but which may also be due to the secondary metamorphism being drawn out over time. Temperature estimates are constrained by garnet-phengite geothermometry in oxidised assemblages with Mn-rich garnets to be between 450 and 530°C, the higher temperatures obtained from a rock preserving an earlier-formed fabric. The pressures were at least 8 kbar, based on minimum estimates from assemblages whose fabrics are relatively late in the textural evolution of the secondary assemblages. Towards the end of the secondary metamorphism, temperatures were about 300 to 350°C, based on the presence of chlorite-k-feldspar bearing assemblages. Pressures at this time were about 6 kbar, again poorly constrained due to disequilibrium.

The correlations between grade, temperature, pressure and exposed structural depth are best seen to the north-west of Tarbert, because the rocks to the south-east are overprinted pervasively by secondary metamorphism. However, high pressures from relict primary assemblages from Northern Kintyre, suggest that the correlation between structural depth and pressure continues. In addition, the evidence for relatively high temperatures during the early stages of the secondary metamorphism suggests that the rocks in Northern Kintyre may have been at a comparable temperature to those at Tarbert during the primary metamorphism, although there is no quantitative constraint on the Northern Kintyre assemblages. One assemblage from Northern Kintyre does contain relics of almandine-grossular garnet, with higher Mg/Fe ratios than the highest grade garnets seen near Tarbert, and is therefore consistent with the suggestion that metamorphic temperatures continued to increase to the south-east of Tarbert. As a result, the rocks which experienced maximum temperatures of metamorphism roughly equivalent to the garnet isograd in North Knapdale will lie some way to the south of Tarbert, and possibly to the south of the Cowal Antiform fold axis.

Finally, the rocks in which secondary metamorphic assemblages were developed were still hot relative to their probable primary metamorphic temperatures, and were at deep structural levels, probably resulting in slower rates of cooling than in similar rocks to the north-west and south-east. These rocks,
being warm and quartz- and layer-silicate-rich are therefore most likely to be deformed (cf. chapter 2).

The deformation associated with the early secondary metamorphism has been argued in chapter 4 to be associated in time and style to the D₃ deformation in the Central Highlands. There, the crust was reaching its peak of metamorphism at this time, while the crust in the South West Highlands had already started to cool. As a result, the assemblages developed during D₃ deformation in the South West Highlands are probably retrograde in nature. All these considerations strengthen the suggestion made in chapter 2 and by Graham (1986) that the thermal regime controlling the regional heating and cooling of the crust would have been different in the South West Highlands to that in the Central Highlands.

The next chapter is devoted to constraining the cooling rates quantitatively in differing parts of the area, as well as timing both the climax of primary metamorphism and the secondary metamorphism in the South West Highlands. These time constraints, will then be compared to other, similar constraints in other parts of the Scottish Dalradian.
CHAPTER 6
TIME CONSTRAINTS ON THE REGIONAL METAMORPHISM:

"When I do ask white Age he saith not so:"

Wilfred Owen, The End

The pressure-temperature histories for Dalradian in the South West Highlands have now been elucidated, constraining significant proportions of their P-T-relative time paths. The primary regional metamorphism was a high pressure "Barrovian" event resulting in biotite and garnet zone assemblages under pressure-temperature conditions of 430 to 550 deg. C and 10 to 12 kbar. The variation in measured P-T conditions from given assemblages, along with some of the mineral chemistry described in previous chapters suggests also that temperatures in the crust at higher grades remained high, and may have continued to rise, for some time after the primary metamorphism.

The higher pressures and temperatures are found in rocks at deeper structural levels, and which were probably buried deeper in the crust during the primary metamorphism. The primary metamorphism was then followed by a more localised, but pervasive, secondary event, affecting mainly the deeper structural levels that probably experienced the highest grades of primary metamorphism. The secondary event occurred during a major deformational episode. This was developed on a regional scale, but no folds affecting the exposure of regional stratigraphy have been recognised so far. A later, more localised, retrograde event affected the more reactive lithologies. Pressure-temperature conditions for the secondary metamorphism were up to 500 deg. C, possibly higher, and 8 kbar for the earlier stages, and 350 deg. C and 6 kbar for the later stages.

This chapter aims to impose absolute time constraints on the metamorphic history of the South West Highlands by radiometric age dating. A number of radiometric cooling age determinations (Dodson 1973, 1979, section 6.1) have been made on micas and amphiboles from samples collected from South West Jura, Tayvallich, Knapdale and Northern Kintyre (Fig. 6.1). When these are added to the information on the changes in P-T conditions that have occurred over time, comprehensive constraints on the P-T-t histories will result. Models of
Fig. 6.1 Location map of the South West Highlands with samples used for geochronology:
the contrasting P-T-t histories will then, in the following chapter, attempt to reproduce the information derived in this and previous chapters, with the aim of finding the main controlling factors of the regional metamorphism in the South West Highlands.

Firstly, the principles, assumptions, and methods used for geochronology in metamorphic belts will be discussed. While most geochronology is carried out to gain information on the times of formation, emplacement, or deposition, of rocks, geochronology in metamorphic rocks usually gives times of cooling from the peak temperatures of metamorphism. Only in exceptional cases, to be discussed below, is information on the times of the peak of metamorphism likely to be available. Thus, the methods, assumptions, and problems concerned with age dating in metamorphic belts are different to those in other fields, and are worthy of detailed discussion prior to the presentation of results and their interpretation.

After the discussion of geochronology and regional metamorphism, the results from this study will be presented and compared with the results of geochronological and P-T-t studies from other areas in the Dalradian. As a result, reconstruction of P-T-t histories of metamorphism in the South West Highlands, one of the main aims of this study, will be complete.

6.1 Methods and Principles of Geochronology Applied to Metamorphic Rocks:

This section presents a discussion of the methods and assumptions involved in geochronology in metamorphic belts. Firstly, a brief historical review of the subject will be given, followed by a description of the closure temperature concept, along with apparent examples where this concept appears to be insufficient to explain observation. However, it will be shown that the concept can be seen to hold good in these cases, if assumptions concerning the behaviour of rocks during and after metamorphism are acceptable. For further information on geochronology in metamorphic rocks, see Cliff (1985).
6.1.1 Geochronology in Metamorphic Rocks; the Historical Perspective:

Since the early 1960's, attempts to measure the absolute time of metamorphic processes have been made by geochronological methods. These have concentrated largely on the dating of separated minerals, because this procedure removes the ambiguities behind the determination of the timing of metamorphism by whole-rock methods. The whole-rock isochron method (eg Leggo et al. 1968, Brewer et al. 1979) depends on the assumption that isotopic homogenisation occurs over the distance scales on the same order as the sampling area. Inspection of metamorphic rocks often produces evidence of chemical and textural disequilibrium over thin section scales or smaller, while isotopic disequilibrium over hand-specimen scales has also been documented, even when fluid/rock ratios were high. This has been put to good use in the timing of polychronic events (eg Cliff et al. 1985). As a result, whole-rock isochron dating cannot unambiguously distinguish between times of emplacement or deposition and times of metamorphism.

K-Ar whole-rock dating is, however, easier to justify, since only one sample is needed to produce an age datum, but the K-bearing phases obviously need to have grown only during the metamorphism concerned (eg Harper 1967). Dating of minerals from single hand specimens that have grown in textural equilibrium during a specific metamorphic episode removes the potential ambiguity associated with whole-rock methods.

The first attempts at dating metamorphic and thermal overprinting events produced discordant ages. In regional metamorphic belts, such as the Swiss Alps, controversy ensued as to whether the discordant ages represented times of polychronic mineral growth, or whether the results were due to closing of the minerals with respect to the geochronometers concerned at different stages in the cooling history of the rocks (Jager 1973, 1979, Steiger 1967: see also Deutsch and Steiger 1985). The latter interpretation is now favoured for many reasons. Firstly, the sequence of ages from application of geochronometers to different minerals was usually the same, and independent of the areas studied, and the metamorphic and textural histories of the rocks concerned. Secondly, studies of contact metamorphic aureoles, removing possibilities of polychronic metamorphism, gave a similar sequence of ages from the systems used to that derived from regional metamorphic belts. (Hart 1964, Hanson and Gast 1967). Thirdly, mineral ages
were reset as a result of re-heating only when the assemblages developed during the re-heating exceeded given, specific grades. (Purdy and Jager 1979).

As a result, mineral ages were interpreted in terms of blocking temperatures, at which the free exchange of daughter products of radio-active decay ceased as the rocks cooled. Implicit in this concept are the suggestions, first that the opening temperature during heating, above which free exchange will occur, is equal to the blocking temperature; thus that exchange is switched on and off very quickly at the blocking temperature (Zeitler and Wijbrands 1886), and second, that temperature changes are the dominant mechanism for the resetting of ages, unless mineral growth occurs below the supposed blocking temperature.

The blocking temperature concept was refined by the models of Dodson (1973, 1979) which used Fick's Laws of diffusion to model the rapid closure of systems in which diffusion obeys an inverse exponential (Arrhenius) relationship with temperature. Thus, the blocking temperature model, implying very rapid resetting of the system concerned at a fixed temperature whereby opening and closure occurred at the same temperature, was replaced by the closure temperature concept in which opening and closure occurs at differing temperatures. The model considered the exchange of a species between a grain and an infinite reservoir. On the Arrhenius plot (Fig. 6.2), the slopes of diffusion rate v. temperature are given by the activation energy for the diffusion process. In silicate minerals, activation energies are often, but not always, large. If the activation energies are large, their Arrhenius slopes are steep, so the rates of diffusion are very sensitive to temperature.

In the case of radioactive decay, the apparent age given by a geochronometer is the time elapsed since the concentration of the daughter product was zero. At high temperatures, the rate of loss of the daughter product in a mineral is faster than the rate of accumulation. As the modelled system cools, however, the rate of loss decreases rapidly. At a temperature \( T_q \) (Fig. 6.3), the rate of loss is low enough that the exchanging species starts to accumulate. At, or below, temperature \( T_0 \), the rate of loss is very close to zero, so no significant loss occurs. In a system whose activation energy is high, the temperature interval, \( T_q - T_0 \), is small, and the temperature range bracketed by \( T_q - T_0 \) approximates to the closure temperature of the system, \( T_c \), given formally by the apparent temperature at which the concentration of the exchanging species is zero. \( T_c \) is found by extrapolation of the line on Fig. 6.3(b) of concentration against time, to \( D/P = 0 \)
Fig. 6.2 Generalised Arrhenius relationships of two temperature-dependent processes: the activation energy of each process is given by the slope of the straight line.
Fig. 6.3 The closure temperature model: above $T_Q$, the rate of loss by diffusion is high and the rate of accumulation is low. At $T_0$, the rate of loss is low, while the rate of accumulation is high so that the $D/P$ ratio increases along an approximately straight line. The closure temperature, $T_c$, is given by the extrapolation of the straight line to $D/P = 0$, and the cooling age, $t_c$, is given by the time elapsed since $D/P = 0$ (after Dodson 1973, 1979 and Ganguly and Ruiz 1987).
According to Dodson (1979), the closure temperature of diffusion for a species is given by

\[ T_c = \frac{E}{R} \cdot \frac{1}{\ln(AD_0T^*/a^2)} \cdot \left(\frac{RT_c^2}{E}\right) \]

where \( E \) is the activation energy of diffusion, \( D_0 \) is the frequency factor, or the conceptual diffusion rate at infinitely high temperature, \( A \) is a geometrical constant for the diffusion; for a spherical diffusion model, \( A = 55 \), and for cylindrical diffusion, \( A = 27 \), \( T^* \) is the cooling rate of the system, \( R \) is the gas constant, \( a \) the effective diffusion distance (see 6.1.2 and 6.1.3), and \( T_c \) is the closure temperature. \( T_c \) appears on both sides of the equation, so its value is found by iteration. Convergence to ±5°C results within three iterations.

The size of the temperature interval, \( T_q - T_0 \), is not known for most mineral geochronometers, due to the absence of diffusion parameters, but Ganguly and Ruiz (1987), based on diffusion data for other species and minerals with similar activation energies, suggest that this interval is less than 50°C. Clearly, the closure temperature in this model depends on cooling rates, increased cooling rates giving higher closure temperatures. Dodson (1979) calculates, using the closure temperature equation, that order of magnitude changes in cooling rates give differences in closure temperatures of about 10 to 20°C. Since the closure temperature can only vary between \( T_0 \) and \( T_q \) on Fig 6.3, these changes in the value of \( T_c \) agree with the estimates of Ganguly and Ruiz (1987) for the interval \( T_q - T_0 \).

The other influence on closure temperature is the effective distance of diffusion, which is the average distance travelled by atoms or molecules of a diffusing species between its point of origin and the reservoir with which exchange is taking place, where its concentration is close to zero. This is usually taken to be equivalent to the grain size of the exchanging phase, giving rise to apparent contradictions to the closure temperature concept when relationships between ages and grainsizes fail to materialise (section 6.1.2).

The main difference between blocking temperatures and closure temperatures is that while the former are said to be fixed, the latter are variable, being dependent both on cooling rates and effective distances of diffusion. As a result the statement "the closure temperature of species X in mineral Y is..." is meaningless, since it implies a unique value of the closure temperature. Fig. 6.4
Fig. 6.4 Variation of closure temperatures of Ar diffusion in hornblende, based on the data of Harrison (1981) (from Cliff 1985):

\[ D_p / D_1 = m = (e^{\lambda t} - 1) \]

Fig. 6.5 Generalised isochron relationship for a suite of samples that were in isotopic equilibrium at time, 0: the slope of the line gives the time since isotopic equilibration.
shows how closure temperatures can vary with effective diffusion distances and cooling rates. In addition, the model of Dodson (1973, 1979) implies that the closure temperature will not be equal to the opening temperature, at which a geochronometer is reset. For resetting to occur, the concentration of the daughter product has to be zero, so almost complete exchange needs to occur. Kinetics make it inevitable that the opening temperature of a system will be higher than the closure temperature of the same system, so the closure temperature needs to be exceeded before resetting can occur unless the time-scales of the heating and cooling processes are long. All the above points need to be borne in mind when considering the apparent contradictions to the closure temperature concept to be discussed in the next subsection.

6.1.2 The Closure Temperature Concept; Is It Consistent?:

It is not surprising that a relatively basic and simple model such as that outlined above for closure temperatures has proved to be controversial. Two studies that gave observations that were apparently contradictory to the closure temperature concept are Verschure et al. (1960) and Chopin and Maluski (1980). Both these studies presented evidence that rocks had been heated above "accepted" (rigidly defined) closure temperatures for two different mineral geochronometers, but older ages were still preserved, the geochronometers having failed to reset during the re-heating phases.

The first of these studies, that of Verschure et al. (1980) cited the growth of biotite which gave Caledonian K-Ar ages in rocks in which Grenvillian ages in biotite were preserved. The younger biotite was green and grew at the expense of the older, brown biotite. Older biotites co-existed with younger biotites in a zone separating green (young) biotite-bearing rocks from brown (old) biotite-bearing rocks. This study suggested, based on a supposed lower temperature stability limit of biotite of ca. 400°C, that the rocks had been heated to a higher temperature than the "accepted" closure temperature for Argon in biotite (ca. 300°C, section 6.2) but that because older biotite had not been reset, the closure temperature was either higher, or that the closure temperature concept was mistaken.

The other study, that of Chopin and Maluski (1980) presented the observation that texturally old, high pressure celadonite-rich phengites preserved older Ar-Ar ages, (eg Dalrymple and Lanphere 1974) while young, lower pressure, more
muscovite-rich phengites gave young ages, using the same geochronometer. This was despite the observation that the young phengites grew at temperatures about 100°C higher than the "accepted" closure temperature for Ar in phengite (ca. 350°C, section 6.2). As a result, both of these studies reach similar conclusions, namely, the failure of the geochronometer to reset, despite the rocks being heated to temperatures apparently much higher than the closure temperatures concerned.

As far as the Verschure et al. study is concerned, its conclusions depend on the lower temperature stability limits of biotite in K-feldspar-bearing assemblages. As described at length in chapter 5, this temperature has been bracketed approximately by Massonne and Schreyer (1987) in the Fe-free system at temperatures of 300 to 350°C, and is likely to be displaced towards lower temperatures in Fe-bearing systems (section 5.1). As a result, the rocks studied by Verschure et al. (1980) probably did not reach high enough temperatures to cause complete resetting of the Ar systems in the older biotites. The data presented by Verschure et al. indicate that some Ar loss did occur, because the old biotites in partially over-printed assemblages were ca. 100 ma younger than those in rocks that only had older biotites present.

The study of Chopin and Maluski (1980) is not so easy to explain, since the temperatures attained during the reheating were ca 100°C higher than those assumed for the closure of Ar diffusion in phengite. Chopin and Maluski suggested that diffusion obeying Fick's laws was not operating at all, but that the isotope systems were re-set when reaction in the assemblages ceased. This meant that those assemblages in which reaction had not occurred preserved their old ages, not because they had not exceeded the appropriate closure temperature, but because there had been no chemical reaction to cause resetting. However, these observations can, in principle, be explained within the Dodson model for cooling ages. Three such possible explanations are:

1. The sealing-off mechanism invoked by Chopin and Maluski had the effect of increasing the effective diffusion distance of the system so that it was of much greater length-scales than the average grain size. I emphasise again that, in the closure temperature model, the effective diffusion distance is the average distance travelled by a diffusing species between the source and the infinite reservoir with which it is exchanging. Normally this will be less than, or equal to, the grain size, but conceptually, the diffusion distance may be larger than the average grain size of the exchanging phase. This possibility is explored further in 6.1.3 below.

2. The closure temperature for Ar diffusion in a celadonite-rich phengite is greater than that for a more muscovite-rich phengite.
3. The difference between the closure temperature and the opening temperature of Ar diffusion in phengite is high enough that the phengites were not reset during the overprinting metamorphism.

None of these possibilities are constrained at present, due mainly to the absence of diffusion parameters for differing phengite compositions. Very few experiments have been carried out for Ar diffusion in phengites (eg Robbins 1974), and the parameters derived by Monie (1986) are based on non-hydrothermal measurements of outgassing of irradiated phengites, carried out during Ar-Ar dating. It is unlikely therefore, that these parameters are directly applicable to natural rocks. Calculation of closure temperatures (table 6.1) for Ar diffusion in phengite based on Robbins' parameters suggests that effective diffusion distances influence the resulting values very strongly. In the mechanism postulated by Chopin and Maluski, the ending of chemical reaction will coincide with the fluid leaving the rock resulting in a slowing-down of the transport rates through the assemblage. The possible effects of varying fluid/rock ratios on closure temperatures is considered further in 6.1.3 below.

An additional consideration is the rate of temperature change during a resetting episode. Remembering that an increased cooling rate increases closure, and hence opening, temperatures, the preservation of blueschist facies assemblages suggests that heating and cooling rates were high (Draper and Bone 1981, chapter 7). Though the high heating/cooling rates necessary to preserve blueschists probably would not be sufficient on their own to prevent resetting of the Ar system in phengites, they will make such resetting more unlikely than in a terrain that has heated and cooled slowly.

6.1.3 Conclusions; Refining and Defining the Closure Temperature Concept:

Subsection 6.1.2 should make it clear that observations that apparently contradict the theory of cooling ages, as modelled by Dodson (1973, 1979), can in fact be made consistent, simply by accepting the notion that effective diffusion distances need not be equivalent to grain sizes. It would normally be accepted that effective diffusion distances can be smaller than the average grain size of the exchanging minerals, but the observations cited above require that effective diffusion distances be larger than the average grain size, if they are to be explained in terms of the closure temperature theory. The problem therefore
Table 6.1 Calculated closure temperatures (°C) for Ar diffusion in muscovite, with varying effective distances and cooling rates, using the experimental parameters of Robbins (1972):

<table>
<thead>
<tr>
<th>Effective distance (cm)</th>
<th>0.01</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>350</td>
<td>450</td>
</tr>
<tr>
<td>3</td>
<td>375</td>
<td>475</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 6.2 Hydrothermal diffusion data available at the time of writing for some of the phases discussed in this chapter:

<table>
<thead>
<tr>
<th>Authors</th>
<th>Mineral</th>
<th>Species</th>
<th>$Q$ (kcal Mol$^{-1}$)</th>
<th>$D_0$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hofmann and Giletti (1970)</td>
<td>Biotite</td>
<td>Rb</td>
<td>21</td>
<td>2.1 E-10</td>
</tr>
<tr>
<td>Giletti (1974)</td>
<td>Phlogopite</td>
<td>Ar</td>
<td>57.9</td>
<td>0.75</td>
</tr>
<tr>
<td>Harrison et al. (1985)</td>
<td>Biotite</td>
<td>Ar</td>
<td>47</td>
<td>0.077</td>
</tr>
<tr>
<td>Harrison (1981)</td>
<td>Hornblende</td>
<td>Ar</td>
<td>64.1</td>
<td>0.024</td>
</tr>
<tr>
<td>Robbins (1972)</td>
<td>Muscovite</td>
<td>Ar</td>
<td>40</td>
<td>6.03E-07</td>
</tr>
<tr>
<td>Giletti (unpubl.)</td>
<td>Albite</td>
<td>Sr</td>
<td>56</td>
<td>0.014</td>
</tr>
<tr>
<td>Giletti (unpubl.)</td>
<td>Orthoclase</td>
<td>Sr</td>
<td>42</td>
<td>3.63E-06</td>
</tr>
</tbody>
</table>
concerns the effectiveness of transport mechanisms in rocks which are petrologically inactive (i.e., in which no metamorphic reaction is occurring). The closure temperature concept, by definition, does not time the ending of metamorphism, but the ending of exchange of a species by diffusion. Thus, the use of the closure temperature concept to explain geochronological results infers that the ages do not time metamorphic events.

A study that illuminates the problem of transport mechanisms in rocks is that of Walther and Wood (1984) who considered the rates of dissolution and nucleation of phases, and transport of reactants during metamorphism, in a semi-quantitative model. These authors concluded that dissolution and precipitation can occur rapidly over <1000-year timescales, based on known dissolution data. In comparison, the time-scales of transport mechanisms were shown to be substantially slower. Thus, the rate limiting step for a metamorphic reaction is the rate at which chemical components are transported through a rock during metamorphism.

Walther and Wood (1984) made the assumption that transport in a rock occurs dominantly in the grain boundary region, this being defined as the disordered part of the rock, by one or more of three mechanisms. These were: fluid flow through microcracks and grain boundaries, diffusion of solutes through a fluid lying within a grain boundary region, and diffusion though a grain boundary region in the absence of a fluid. All three of these mechanisms will occur within a given rock, but their relative importance depend on the environment (amount of fluid, temperature, width of grain boundaries) of metamorphism, each one of these mechanisms being the dominant mode of transport under given conditions. The models showed the following:

1. Fluid flow is an important transport mechanism when the instantaneous fluid/rock ratio is relatively large, and there is much fluid present in grain boundaries and microcracks.
2. Diffusion through fluid in grain boundaries is the dominant mechanism when the instantaneous fluid/rock ratio is smaller. This occurs when the fluid flow rate, driven by buoyancy forces at deep levels in the crust, is limited by the fluid viscosity.
3. Grain boundary diffusion as a transport mechanism is only significant when the instantaneous fluid-rock ratio is very small, and when the temperatures of metamorphism are relatively high.

This model is originally intended for consideration of the processes that occur
in a rock during metamorphism, but it is also applicable to the problem of exchange of a diffusing species between a grain from which the species is diffusing, and a reservoir defined by the rest of the surrounding rock, when modified to account for volume diffusion within grains. This is because the exchange with the reservoir necessarily involves transport of the diffusing species away from the grain being considered.

The modification of the Walther and Wood (1984) model for volume diffusion is necessary because for a geochronometer system to be open, volume diffusion of the radiogenic species must occur at a high enough rate that loss by diffusion exceeds gain by radioactive decay. Exchange of the radiogenic species between the phase of interest and the surroundings occurs either as a result of one of the three grain boundary transport mechanisms of Walther and Wood (1984), or by volume diffusion within the other phases in the assemblage. The exchange of the radiogenic species ceases when transport in the surroundings, or volume diffusion in the phase, no longer occurs at a significant rate.

In this discussion, metamorphism is taken as being the presence of dissolution and recrystallisation of minerals in a rock, or the presence of "petrological activity" (Chopin and Maluski 1980). As discussed in chapters 3 and 4, metamorphism needs one, or both, of excess fluid and deformation to occur, and the time-scales of dissolution and recrystallisation are probably on the order of 1 E 03 to 1 E 05 years (eg Ridley 1985). Thus, petrological activity in rocks now at the surface probably takes place only over small parts of the rocks’ P-T-t paths.

Consider, therefore, a metamorphic grain in which a radiogenic species is exchanging freely with its surroundings. The rate of transport of the species away from this grain depends on which of the three mechanisms listed above, and volume diffusion, is the most important, and on the conditions and environment of metamorphism. During a metamorphic episode in the presence of a fluid, taking place at $T > T_c$ (where $T_c$ is the closure temperature for the geochronometer), transport of the species away from the grain will be rapid, and will take place by advection by the metamorphic fluid. Thus the rate-limiting step is the rate of volume diffusion of the species in the grain. In this case, the effective diffusion distance will be no larger than the average grain size of the mineral concerned, and will probably be smaller.

After a while, metamorphism, or petrological activity, ceases in the
assemblage. There are three main reasons why this may be so:

1. the reactions concerned have gone to completion,
2. fluid movement through the rock has ceased,
3. deformation has ceased.

The first of these reasons will only be significant if no continuous exchange reactions are occurring, while the other two reasons imply the role of fluid and deformation in the catalysis of metamorphic reactions. The need for catalysis is almost universally accepted, simply because of the overwhelming evidence for petrological activity in the presence of fluid and deformation. Fluid present during metamorphism is either externally derived, as a result of regional infiltration (e.g., Ferry 1984) or internally derived as a result of breakdown of reactants. In either of these cases, when metamorphism ceases, the instantaneous fluid/rock ratio will be lowered, possibly by orders of magnitude, or a free fluid phase, in the thermodynamic sense, will disappear, and transport of the diffusing species from the grain to the surrounding reservoir will therefore be slowed down, since this will now probably occur either by diffusion through the fluid remaining in the intergranular region, or by diffusion through the grain boundary in extreme cases.

As a result, though the temperature of the rock may be still higher than the closure temperature for the volume diffusion of the radiogenic species, exchange of the species with the surroundings is made harder by the slowing-down of transport through the surroundings (whether this occurs by grain boundary transport, or by volume diffusion through other phases). Therefore the time taken for a diffusing species to reach the reservoir with which exchange is occurring is longer than the time to reach the reservoir when metamorphism was occurring. The effective diffusion distance is therefore increased, and the closure temperature of the geochronometer (not the volume diffusion of the species in the mineral) is raised.

Thus far, the discussion has been generalised, not specific to particular mineral-geochronometer systems. In more specific terms, three geochronometers are most commonly used in metamorphic rocks: Rb-Sr, Ar-Ar and K-Ar. The diffusing species of interest is therefore usually either Sr or Ar. While Ar is inert, and can therefore be considered as behaving like a fluid, Sr needs to be considered as a solute. As a result, free movement of Sr through a rock may
depend on the presence of a fluid phase in grain boundaries, while the exchange of Ar between a grain and its surroundings is made easier by the fluid, and therefore, mobile state of Ar. Despite the probable mobility of Ar, the two examples of observations cited above (6.3.2), that are apparently contradictory to the closure temperature theory, both involve Ar diffusion.

As yet, the actual values of closure temperatures of differing diffusing species in different minerals has not entered the discussion in detail. It will become clear that, taking the closure temperature estimates at face value, most grades of metamorphism represent temperatures greater than the closure temperatures concerned. As a result, volume diffusion through ordered grains is a significant additional transport mechanism at \( T > T_c \). In addition, most closure temperature intervals \( (T_q - T_0) \) will be crossed after metamorphic reactions in the rock have ceased. If, however, the other phases in the rock are closed to the diffusing species concerned, exchange will only occur with the grain boundary region. As a result, the exchange of Ar between a mineral and its surroundings is again made conceptually easier than the exchange of Sr. If volume diffusion of Sr in a given phase has a relatively high closure temperature, exchange with the surroundings at \( T > T_c \) may be enhanced by two factors:

1. increased diffusion rates (which will be temperature-dependent) through grain boundaries or grain boundary fluids.
2. The greater probability that volume diffusion in other minerals in the assemblage will occur.

In contrast, a phase in which the volume diffusion of Sr has a low closure temperature may well find exchange with the surroundings harder; grain boundary diffusion will be slower at \( T > T_c \) and volume diffusion may well have closed in the other phases in the rock.

As a result, dating a mineral with the Rb-Sr system, in which Sr-diffusion has a low closure temperature is, conceptually, problematic. The phase in the assemblage with the lowest closure temperature will close when the phase with the second lowest closure temperature closes, because it has nothing else to exchange with, unless significant exchange with the grain boundary region can occur. Unpublished diffusion parameters for Sr diffusion in albite (Giletti 1988, pers. comm.) give closure temperatures of 500 to 550°C for regional metamorphic cooling rates and 0.1 to 1 mm effective diffusion distances (tables 6.2 and 6.8).
Orthoclase has a similar closure temperature for similar effective diffusion distances according to the data on table 6.2, but it could be argued that, due to exsolution etc, effective distances in this phase will be lowered considerably, thus lowering closure temperatures. As a result, biotite co-existing with an assemblage with high modal phengite and albite will close at a higher closure temperature than biotite co-existing with k-feldspar (see also section 6.3.4).

Similar conceptual problems will not be faced to the same extent by Ar-based dating methods, nor by Sr-based methods with higher closure temperatures. I stress that the problems cited are conceptual; the observations made numerous times over the years imply that Rb-Sr dating of biotites gives consistent, and similar results in most cases. Some of these observations have been made in this study. Other observations, also made in this study, are apparently contradictory, but will be shown to be an artifact of errors in the methods used to calculate Rb-Sr ages becoming significant in certain cases (see also Dempster 1986), these errors being due to the closure of Sr-bearing phases at $T > T_{c-bi}$ altering the compositions of the exchanging reservoir. The next section describes the methods used in this study, and other studies, to calculate mineral cooling ages.

**6.2 Geochronological Methods:**

Having reviewed the closure temperature theory and model, the geochronological methods used in this study are now examined in the light of the conclusions drawn in the previous section. This section will include the derivation of closure temperature values, and their possible variation in regional metamorphic rocks (based on possible cooling rates, mineral compositions, and effective diffusion distances) as well as the methods used to evaluate these closure temperatures. Practical methods (sample preparation and running conditions etc... are described in appendix I. Following this, the calculation of mineral ages from the isotopic data will be discussed, along with the potential sources of error, and their possible magnitude.

Closure temperatures can be measured either by empirical comparison with well-characterised natural rocks, or by direct experiment. The first measurements of closure temperatures were empirical, based on studies in the Swiss Alps (eg Purdy and Jager 1976), as well as in studies of contact aureoles (Hart 1964,
Hanson and Gast 1967). In these studies the grades at which resetting of older to younger mineral ages occurred were used to assign blocking (as opposed to closure) temperatures. In studies of regional metamorphic rocks, no attempt was made to derive the necessary diffusion parameters for formal calculations of closure temperatures to be made, mainly because the cooling histories of the rocks concerned could not be modelled in a rigorous way. In contrast, the cooling of intrusive bodies is relatively easy to model thermally, so that estimates of diffusion parameters could be made for each of the age dating systems used (e.g. Hart 1964).

Experimental calibrations of mineral geochronometers are relatively scarce and often non-rigorous. Giletti (1974) defined the criteria for good experimental practice, criteria which have not always been adhered to in subsequent studies. The minerals used for age dating in metamorphic rocks are usually hydrous, so experiments should be run under hydrothermal conditions, otherwise the mineral may be unstable, and the transport mechanism being measured may not be the volume diffusion that would occur in nature. The initial abundance of the products of radioactive decay must be well-characterised and their distribution should be homogeneous. Finally, the effective diffusion distance of the element in the sample used should be characterised; one way of doing this is to use gently crushed and sieved size fractions, the experimental data from these being compared with one another.

Good examples of experimental practice are found in the studies of Harrison and co-workers (Harrison 1981, Harrison et al. 1985) of the diffusion of Ar in hornblende and biotite, in Hoffmann and Giletti (1970), for Rb diffusion in biotite, and Giletti (1974), for Ar diffusion in phlogopite. In the experiments of Harrison and co-workers, standard samples are hydrothermally heated and their total Ar concentrations at the end of the heating measured. Obviously, temperatures and durations of each run are well constrained. Aliquots of each sample are also dated using the Ar-Ar technique, to characterise the distribution of Ar in the samples used. The Ar distribution was found to be homogeneous, since flat plateaux resulted. This method avoids the destruction of the mineral lattice by irradiation and by non-hydrothermal heating; the mineral used in the experiment represents the mineral in nature. Effective diffusion distances measured by the studies of Harrison and co-workers for both biotite and hornblende are about 0.01 to 0.015 cm. Diffusion parameters from these
experiments are summarised on table 6.2.

The two age dating systems used in this study were K-Ar and Rb-Sr dating, mainly in phengite and biotite. In addition, amphiboles from some of the many metabasic assemblages in the area were dated by the K-Ar method. Each of the five mineral dating systems that result will be considered in turn.

6.2.1 K-Ar Dating; Closure Temperature Evaluation:

K-Ar dating is based on the decay of $^{40}$K to $^{40}$Ar, this being part of a more complex branching decay; details are found in Faure (1978). Since K is very abundant in terrestrial metamorphic rocks, this geochronometer has been evaluated and developed for some time (eg Holmes et al. 1955), and is applicable to a wide range of rocks and minerals. In the case of metamorphic minerals, micas will often have up to 8 weight % K, so this method is particularly well suited to these minerals. Amphiboles are less abundant in K than micas, so ages from these minerals are subject to larger error.

6.2.1.1 Phengites; Constraints on Closure Temperatures:

Most studies involving K-Ar or Ar-Ar dating on phengites use the empirical calibration of the closure temperature of Purdy and Jager (1979). This calibration, based on comparison of ages from phengites with K-Ar and Rb-Sr ages of biotites, resulted in a closure temperature value of ca. 350°C, but with a relatively large error. Relatively little attempt has been made to calculate diffusion parameters for Ar in phengite, examples being Monie (1986) and Robbins (1972). The former study used irradiated natural samples and non-hydrothermal step-heating measurements, therefore not conforming to good experimental practice. The latter study is not published, but was in collaboration with Giletti’s group, so is likely to conform to Giletti’s (1974) criteria. However Giletti (1988, pers. comm.) advises that Robbins’ data are sparse, and the diffusion parameters are therefore subject to large error.

Use of the closure temperature expression of Dodson (1979) and the parameters of Robbins (1972) results in a closure temperature range of ca. 350 to 500°C for cooling rates of 1, 3, and 10°C Ma$^{-1}$, and effective diffusion distances of 0.01 and 0.1 cm (table 6.1). Taking Robbins’ data at face value means that the
closure temperature for Ar diffusion in phengite will be higher than 350°C even in slowly cooled regional metamorphic terrains, and higher still in contact metamorphic rocks. As a result, the available constraints on the closure temperature for Ar in phengites give a range of between 350 and 400°C, and this range in closure temperature values has been adopted in this study. Due to the paucity of experimental data, it is unclear what effect compositional variation has on closure temperatures in phengite.

6.2.1.2 Biotites; Constraints on Closure Temperatures:

The constraints on the closure temperatures of Ar diffusion in biotite are better than for phengite, due to the greater number of experiments that have been carried out, especially by Harrison (1985), and Giletti (1974(b)). These experiments show that the closure temperatures in biotite depend strongly on composition, with greater retentivity (higher closure temperatures) in Mg-richer compositions. The diffusion parameters of Harrison (1985) for biotite of \( X_{Fe} = 0.56 \) lead to closure temperatures of about 300 to 360°C depending on cooling rates and diffusion distances, with the effective diffusion distance of diffusion characterised by Harrison (1985) resulting in \( T_c \) values of ca. 300°C for regional metamorphic cooling rates. Studies of natural rocks result in similar estimates for closure temperatures in biotites. Since the biotites analysed in this study have \( X-Fe \) values of between 0.35 and 0.65, closure temperature values of 300±50°C have been adopted in this study.

6.2.1.3 Hornblende; Constraints on Closure Temperatures:

The constraints on Ar diffusion in hornblende are relatively good, again due to rigorous experiment. The study of Hart (1964) showed that hornblende was relatively retentive of Ar, while Harrison (1981) assigned closure temperatures of 450 to 500°C for regional metamorphic cooling rates and the experimentally-characterised effective diffusion distance (Fig. 6.4). Harrison’s parameters were in good agreement with those derived empirically by Harrison and MacDougall (1980). While O’Nions et al. (1969) found evidence from age measurements of natural amphiboles that more Mg-rich compositions were more retentive than Fe-rich compositions, no such relationship was found by Harrison (1981). The diffusion measurements from the two differing compositions used in the latter study fitted well on the same Arrhenius relationship.
Evidence for lower closure temperatures than 500°C in amphiboles is found in Harrison and Fitzgerald (1986) who showed that hornblende that has undergone exsolution of cummingtonitic amphibole gave Ar-Ar total fusion ages that were younger than those of co-existing biotite. Harrison and Fitzgerald (1986) also showed that the different types of amphibole had differing retentivities. As a result, amphiboles need to be characterised carefully and evidence for post-growth alteration (chloritisation, exsolution etc.) needs to be looked for, before assigning the 500°C closure temperature to the samples analysed. Thus, specific closure temperatures have not been assigned in this study, but the ages resulting have been compared to those from other minerals. As will be demonstrated, the ages from amphiboles in this study are not consistent with a high closure temperature for Ar diffusion.

6.2.2 Rb-Sr Dating; Closure Temperature Evaluation:

Unlike K-Ar dating, there is little information available on the diffusion of Sr in minerals from direct experiment. Thus, virtually all calibrations are derived empirically. Hoffmann and Giletti (1970) carried out diffusion experiments on Rb in biotite, from which Dodson (1979) calculated a closure temperature of ca. 300°C. This value obviously pertains to the parent isotope and not the daughter product, so the diffusion parameters concerned may not necessarily be appropriate. Giletti (1988, pers. comm.) advises that work in progress on Sr diffusion in biotite suggests a relatively low activation energy for this diffusion, similar to that of Rb diffusion in biotite measured by Hofmann and Giletti (1970).

The major source of information on closure temperatures for Sr diffusion in micas are the studies of Purdy and Jager (1976) and Wagner et al. (1977). The closure temperatures were defined by the temperatures of overprinting metamorphism which resulted in the resetting of the isotopic system of interest. Thus, Rb-Sr ages in biotites were reset in the zone of growth of stilpnomelane during alpine metamorphism, while phengite Rb-Sr ages were reset at higher grades, close to the staurolite to chloritoid transition. Thus, closure temperatures for Sr in biotite were set at 300±50°C, and for Sr in phengite, at 500±50°C. The errors are relatively large, because of the errors associated with the characterisation of the temperatures of metamorphism.

Biotite Rb-Sr ages are usually similar to K-Ar ages from the same phase, the
diffusion of Ar being well constrained by experiment. Hart (1964) calculated similar activation energies for diffusion of both Sr and Ar in biotite, but suggested that biotite is less retentive to Ar than Sr. Similar conclusions were reached by Harrison and MacDougal (1980). Dempster (1986), by analysing biotites with differing chemistry, suggested that activation energies were similar for Ar and Sr, and depended on the mineral chemistry, Sr varying more than Ar. Thus, closure temperatures are probably similar for both Ar and Sr in biotite, at about 300°C, the errors on Ar closure temperatures probably being smaller than those for Sr diffusion, mainly due to the better constraint on the former.

6.2.3 Methods of Calculation of Ages; Assumptions and Problems:

The principle of radiometric age dating is that the ages resulting are the times since the daughter product of the decay started to accumulate in the substance being dated. Therefore, to calculate an age from measurements of isotope ratios requires knowledge of the initial abundance of the daughter product. The equation for radioactive decay is:

\[ D = D_0 + N(e^{\lambda t} - 1) \] (1)

where \( t \) is the time elapsed since accumulation of radiogenic atoms started, \( D \) is the number of radiogenic atoms at time \( t \), \( D_0 \) is the initial number of radiogenic atoms at \( t = 0 \), \( N \) is the number of decaying, parent atoms at time \( t \), and \( \lambda \) is the decay constant.

This equation can be adapted for any decay scheme.

6.2.3.1 K-Ar Age Calculation:

K-Ar geochronology assumes that the initial concentration of \(^{40}\text{Ar}\), the product isotope of the decay of \(^{40}\text{K}\), in the substance to be dated, was zero, so that all of the \(^{40}\text{Ar}\) in the sample analysed is radiogenic. Since Ar is a noble gas, it is inert, so it will not usually take part in chemical reactions, and will tend not to be incorporated into a mineral structure by chemical means. However, the very idea of the closure temperature concept means that systems can remain open for part of their geological history. As a result, if \(^{40}\text{Ar}\) is present as part of the fluid.
phase, and the temperature is sufficiently high, some of this Ar will be incorporated into minerals, by diffusion. This results in excess radiogenic Ar, leading to apparently old ages. Cases of excess Ar incorporation have been recognised in several studies (e.g. Harrison and McDougall 1981). Amphiboles, being poor in K, and hence, radiogenic Ar, are more vulnerable to alteration of their apparent ages by excess Ar uptake, but since they tend to have high closure temperatures, uptake of excess Ar is less likely. In most studies, excess Ar can only be recognised by older-than-expected ages, introducing possibilities for subjectivity. However, excess Ar can usually be recognised by comparison with other age data from the same samples.

6.2.3.2 Rb-Sr Age Calculation:

In contrast to K-Ar dating, the assumption of zero $^{87}$Sr initial concentration cannot be justified because Sr is not gaseous, but will be reactive, and will be incorporated into rocks and minerals. Therefore, initial $^{87}$Sr concentrations have to be known. Equation (1) can be re-arranged to give:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_0 \left(e^{\lambda t} - 1\right)$$  \hspace{1cm} (2)

where $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_i$ is the initial ratio of Sr isotopes, $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_m$ is the measured Sr isotope ratio in the sample, and $\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_p$ is the measured Rb/Sr isotope ratio. Equation (2) is of the form $y = mx + c$, so it defines a straight line whose gradient is:

$$m = (e^{\lambda t} - 1)$$  \hspace{1cm} (3)

As a result, analysis of several samples that ceased mutually exchanging at $t = 0$ gives a straight line whose intercept at $y = \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_0$ gives $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0$, the initial Sr isotope ratio. This straight line is called an isochron (Fig 6.5).

Obviously, isochrons cannot be constructed with one sample, so, for mineral ages, some other way of finding the initial $^{87}$Sr abundance is necessary. Since different minerals will have different closure temperatures, use of a phase with low Rb abundance is not justified because it may cease exchanging with other phases in the rock before, or after, the phase of interest has closed. In other words, use of another mineral to correct for initial $^{87}$Sr abundance requires that
both phases close simultaneously. The other alternative is to assume that the rock in which the mineral is found acts as the reservoir for the isotopic exchange at $T > T_c$. This allows the rock to be a closed system on a metre scale, but an open system on a cm scale. Generally, initial $^{87}\text{Sr}$ is corrected for by analysis of the powdered whole rock from which the mineral is separated.

However, the exchanging, open, portion of the whole rock reservoir will change with time as the rock cools, because different phases close at different temperatures, and therefore at different times (see also 6.3.4). Closure of a phase with high Rb and high radiogenic Sr contents early on in the rock’s cooling history will alter the composition of the reservoir significantly. Later-closing phases will not be exchanging with a reservoir with the same composition as early-closing phases. Thus, in principle, using the same initial Sr isotope correction for both phengite and biotite is not normally justified. In addition, use of the whole rock as a reservoir for phengite is not justified, unless this phase is the first to close. Fortunately, because all of the assemblages, from which phengite was separated and analysed, are pelitic with relatively small modes of albite, the errors introduced by assuming that phengite will be the first phase to close, hence that the whole rock analysis represents the exchanging reservoir closely, will not be great (see also 6.3.4).

Strictly, geochronology with biotite will not be justified using the same whole-rock composition as for the phengite in the rock concerned, based on the previous paragraph. However, biotites are usually very rich in Rb, and therefore become extremely radiogenic in a relatively short time. As a result, the errors induced by using the same whole-rock analysis as was used for the phengite are usually small (Cliff et al. 1985a, 6.3.4 below) though they sometimes become significant in young rocks (Dempster 1986).

6.2.4 Conclusions:

The values for the closure temperatures of each of the five age dating systems used in this study have been constrained as closely as possible, based on the information that is available. The values are presented on table 5.3. Clearly, if a mineral grain grows at a lower temperature than the closure temperature for a given radioactive decay scheme, the age that results from application of this decay scheme is the age of crystallisation. Thus, based on the P-T conditions of 00 300.
metamorphism presented in chapter 5. Rb-Sr ages on phengites should time closely both the primary and the secondary metamorphic events, while the other geochronological systems will constrain the rates of cooling after the primary metamorphism. However, the evidence for high temperatures in the garnet zone subsequent to the primary metamorphism has resulted in additional complexities. These will become apparent during the presentation and discussion of the geochronological results.

6.3 Geochronological Results:

In this section, the results of the geochronological studies made on the South West Highlands will be presented and interpreted in the light of the conclusions drawn about the closure temperature concept and its application in the previous sections. In addition, some of the conclusions from previous sections will be illustrated by the behaviour of the isotope systematics in some of the samples analysed. Though most of the ages calculated from the isotopic analyses are consistent with timing of Dalradian metamorphism, based on previous study, and the depositional ages of the Dalradian and the Old Red Sandstone, some of the results will be shown to be manifestly inconsistent with these time constraints (ca. 400 to 600 Ma ago), the inconsistencies being artifacts of errors in the assumptions made in the methods of age calculation.

Results will be presented for ages from all mineral geochronometers used, the area from which samples were collected being divided into two parts. Knapdale and Tayvallich are areas dominantly affected by the primary metamorphism only, while Northern Kintyre and Tarbert are affected by the pervasive, secondary metamorphism described in chapter 4. These two areas will therefore be discussed separately, then compared with each other, and with the results from studies from other parts of the Scottish Dalradian.

6.3.1 Geochronology in the Dalradian:

To place the geochronological results of this study in context, it is necessary to briefly review the results of other studies on the ages of deposition and metamorphism in the Scottish Caledonides. This is to be carried out here.
6.3.1.1 Past Studies:

In chapter 2, the depositional history of the Dalradian was described, along with the constraints on the ages of this deposition. Essentially, Dalradian deposition started after 750 Ma ago, based on the absence of Morarian ages in Grampian Division rocks (Piasecki and van Breeman 1979, 1983) and was still taking place at 595 Ma ago (Hallday et al. 1988, in press). The Moine, present mainly to the north-west of the Great Glen Fault, but also including the Central Highland Division of Piasecki and van Breeman (1979, 1983), has evidence of wide-spread Morarian tectonothermal activity at about 750 to 800 Ma ago, as well as rather more circumstantial evidence for Grenvillian metamorphism at ca. 1050 Ma ago (eg Brewer et al. 1979). Caledonian metamorphism has overprinted these earlier events pervasively, younging towards the Moine Thrust Belt (Dempster 1985) which was active at ca. 430 Ma ago (Johnson et al. 1985, Kelley 1988).

In the Scottish Dalradian, Caledonian metamorphism has long been recognised, and no other metamorphic events have occurred. Harper (1967) timed the peak of metamorphism near the Highland Border at between 490 and 520 Ma, based on K-Ar whole rock dating of slates. These early studies were extended by Dewey and Pankhurst (1970) into the first attempt to use cooling ages to reconstruct the temperature-time history of the Caledonides. This study concluded that the highest grade areas in the Dalradian cooled later than the lower grades, due to the presence of thermal doming (cf Kennedy (1947, see also section 3.6, and Harte and Dempster 1987). Dempster (1984, 1985) showed, however, that the cooling history postulated by Dewey and Pankhurst (1970) was a simplification, with local variations in uplift rates leading to variable cooling ages, and the higher grade areas cooling earlier than lower grade zones. Dempster (1985) also derived similar ages of metamorphism to Harper (1967) from K-Ar dating of low grade slates. All these studies suggested that the peak of Dalradian metamorphism occurred ca. 490 to 520 Ma ago.

The other main constraint on the timing of prograde Dalradian metamorphism was the study of Pidgeon and Aftalion (1979) who dated zircons from the syntectonically intruded Ben Vuirich granite with the U-Pb method. The resulting age was ca. 514 Ma for the peak of Dalradian metamorphism. Thus, the prograde metamorphism in the Dalradian of the Central Highlands, occurring mainly during the D₃ deformation of Harris et al. (1976) and Harte et al. (1984) is timed at between 490 and 514 Ma ago, and is likely to be diachronous between these two limits. In addition, the metamorphic history of the Central Highland
Region is complex, with several localised episodes apparent; Dempster and Harte (1986) recognised a later high pressure metamorphism associated with the Tummell Steep Belt formation, timed at 460 Ma. Dempster (1985) suggested a timing of ca. 460 to 440 Ma for the D$_4$ deformation, involving the formation of the Highland Border Downbend. The state of knowledge on the timing of Dalradian metamorphism prior to this study is summarised on table 6.3.

Relatively little constraint is available on the timing of metamorphism in the South West Highlands prior to this study. Very few data from this area were quoted by Dewey and Pankhurst (1971). However, an Rb-Sr whole rock errorchron (an errorchron being similar to an isochron, but with greater scatter in the analyses) by Leggo et al. (1969) on low grade schists from Eastern Islay gave results of 540 ± 20 Ma. This errorchron is obviously highly ambiguous, and probably is not trustworthy, especially because it was derived from biotite grade metasediments raising possibilities of detrital phengite causing scatter. Bentley et al. (1988) quote unpublished Ar-Ar ages from amphiboles from igneous intrusions on Colonsay of about 600 Ma, with other Ar-Ar measurements on biotites of 420 Ma (see also sections 2.2 and 7.3).

As a result, this thesis represents the first detailed geochronological study of the South West Highlands. The main purpose of this part of the study is to constrain the cooling history of this region. Normally, high cooling rates are expected in metamorphic terrains which have undergone low- to medium-grade, medium-to high-pressure metamorphism (England and Richardson 1977), but the petrological data (3.3.3, 5.4.2) indicate protracted high temperatures after the growth of the primary assemblages. Hence, quantitative cooling rate estimates from mineral cooling ages are of paramount importance.

The other aim of this part of the study is the timing of the various phases of metamorphism that have been recognised. The primary, isograd-defining, assemblages grew during the D$_1$-D$_2$ deformation (section 3.4), in fabrics axial planar to inclined to recumbent major isoclinal folds of bedding. This deformation occurred as a continuum (Roberts 1974, section 2.2), discrete folding phases resolvable on an outcrop scale, but all these phases having congruent vergences and geometries. D$_1$-D$_2$ deformation was probably therefore a time-marker for the region. Although attainment of T$_{\text{max}}$ across the region may have been diachronous, the growth of the primary assemblages and fabrics would not have been so. Micas are fabric-forming minerals, so dating these with the Rb-Sr method should, given close adherence to the closure temperature theory,
Table 6.3

Chronology of events in the Dalradian Supergroup of the Southern Highlandos

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>Structures</th>
<th>Metamorphism</th>
<th>Uplift</th>
<th>Igneous activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-520</td>
<td>$D_1$ (Tay and Tarfside nappes) and $D_2$</td>
<td>Peak metamorphic temperatures</td>
<td>Local uplift (upper Glen Esk)</td>
<td>'Newer' gabbros 'Older' granites</td>
</tr>
<tr>
<td>520-490</td>
<td>$D_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>460-440</td>
<td>$D_4$ (Highland Border downbend)</td>
<td>Retrograde metamorphism; closure of Rb-Sr and K-Ar systems in minerals of the flat belt</td>
<td>Regional uplift</td>
<td>Granites (NE Highlands)</td>
</tr>
<tr>
<td>410-390</td>
<td>Major faults</td>
<td></td>
<td></td>
<td>'Newer' granites</td>
</tr>
</tbody>
</table>
and no petrological resetting of these ages and systems, give good constraints on
the timing of growth of these fabrics. Temperatures of metamorphism throughout
the South West Highlands did not greatly exceed the estimated closure
temperature for Sr diffusion in phengite, so well-characterised $S_1-S_2$ phengites
should give Rb-Sr ages close to the time of the primary metamorphism in all but
the highest grade assemblages, (Fig. 6.6).

In contrast, secondary deformation and metamorphism is not an unequivocal
time-marker in the local tectono-metamorphic history, because no regional-scale
folds associated with its earlier stages have been recognised (4.2). It has, however,
been suggested that the early stages of secondary metamorphism occurred during
$D_3$ (4.2), which has been timed in Perthshire and Angus at between 490 and 515
Ma ago (Dempster 1985). Thus, Rb-Sr dating of well-characterised secondary
phengite fabrics may act as a test for this argument, by comparison of these ages
with time constraints on $D_3$ elsewhere in the Dalradian.

Ages from other minerals using other geochronometers should be cooling ages,
and should therefore constrain the cooling rates of the region from the time of
last attainment of $500^\circ$C given by the Rb-Sr phengite ages. Thus, ages from $S_1-S_2$
phengites should be greater than the U-Pb age from the post-$D_2$ Ben Vuirich
Granite, while ages from early secondary metamorphic phengites
should be about 500 Ma old (see also Harte 1988).

Rb-Sr ages were calculated in this study correcting for initial Sr by analysing
the whole-rock from which the mineral concerned was separated, hence making
the assumption that this whole-rock analysis represents the exchange reservoir.
The possible errors associated with this assumption are discussed further in 6.3.4,
but essentially, if Rb and Sr are not fractionated strongly between the mineral and
the whole-rock, errors will arise, because analytical error, and error associated
with the assumptions in the age calculation methods, both become significant.
Essentially, if a phengite - whole-rock pair has

$$\left( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_{\text{pheng}} - \left( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_{\text{WR}} < 2.0 \quad (3)$$

the fractionation in Rb and Sr is likely to be too weak to give a meaningful
age (Dempster 1983, p.186). The Rb-Sr fractionation between biotite and the
whole-rock is usually much greater than 2.0, but, even if (3) above is satisfied,
errors may still result due to Sr diffusion in biotite closing later than in most other
pelitic minerals.

Another potential problem is that the whole-rock analysis may be strongly fractionated in Rb and Sr with respect to the mineral, but the whole-rock analysis may not actually represent the real exchange reservoir since, for example, the sample may have been altered or weathered. It is therefore very difficult to objectively decide whether to accept or reject a given age datum, without reference to other age data from the same, or from other studies; ultimately, as with all science, the investigator needs to look first for internal consistency (see also section 1.1) and reject data which cannot be interpreted in any rational way. Such apparently internally inconsistent age data have been derived in this study and will be discussed further in 6.3.4. below.

6.3.1.2 The Present Study; Summary:

The geochronological results of this study are discussed in detail in 6.3.2 and 6.3.3 below, but are summarised here. The previous chapters have shown how the South West Highlands are split into two parts, according to their contrasting tectono-metamorphic histories. The north-west of the area, Jura and Islay, Tayvallich, and Tarbert, is characterised by a relatively straight-forward structural history, accompanied by one phase of metamorphism, this being the $D_1$-$D_2$ deformation and the primary metamorphism, and resulting in one set of planar fabrics, axial planar to folds of bedding. In contrast, the south-east of the study area, Tarbert and Northern Kintyre, shows a complex deformational history, with $D_1$-$D_2$ deformation followed by at least two secondary deformational phases, $D_3$ and $D_4$. $D_1$-$D_2$ and $D_3$ were both accompanied by medium grade regional metamorphism, while $D_4$ accompanied more localised retrograde metamorphism. Each of the sub-sections 6.3.2 and 6.3.3 will deal respectively with these two contrasting parts of the study area. Sampling localities are shown on Fig. 6.1, while the age data are summarised in tables 6.4 and 6.5, and in Figs 6.7 and 6.8.

Rb-Sr phengite ages range between 460 Ma and 524 Ma old, depending on their position across-strike, the younger ages in Tayvallich and in Northern Kintyre, and the older ages in the garnet zone of Central Knapdale. All but two of these ages satisfy (3) above, the exceptions being 85-10 from the garnet isograd in North Knapdale, giving 490 Ma, and JM2 from Tayvallich, giving 474 Ma. All the other phengite ages quoted here have strong enough Rb-Sr fractionation to be deemed acceptable; 85-23 from Central-South Knapdale, whose age of 524±5 Ma
Fig. 6.6 Temperature-relative time history of the South West Highlands, with the estimated range in closure temperatures for the mineral age dating systems used in this study: if metamorphism occurs at $T < T_c$, the resulting age will be the age of the metamorphism, while if the metamorphism occurs at $T > T_c$, the age will be a cooling age.
Fig. 6.7 Across-strike transect for Knapdale and Tayvallich with geochronological data:

- Rb-Sr phengite
- K-Ar phengite
- Rb-Sr biotite
- K-Ar biotite
- K-Ar amphibole

Age (Ma)

Tayvallich Peninsula
Ardishaig Anticline
Garnet isograd
South Knapdale
Tarbert Monoform
Table 6.4 Summary table of isotopic data for Knapdale and Tayvallich: full data listings are given in appendix I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb-Sr age</th>
<th>K-Ar age</th>
</tr>
</thead>
<tbody>
<tr>
<td>84-46 Wr Mu</td>
<td>476±5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JM2 Wr Mu</td>
<td>474±25</td>
<td></td>
</tr>
<tr>
<td>86-22 Wr Mu</td>
<td>464±5</td>
<td></td>
</tr>
<tr>
<td>69-217BH Wr Mu</td>
<td>504±5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86-2 Bi</td>
<td>469±9</td>
<td></td>
</tr>
<tr>
<td>69-204 Act/Hbl</td>
<td>454±9</td>
<td></td>
</tr>
<tr>
<td>69-06 Act</td>
<td>510±12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85-10 Wr Mu</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td>86-10 Wr Mu</td>
<td>498.5±5</td>
<td></td>
</tr>
<tr>
<td>85-11 Bi</td>
<td>444±9</td>
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</tr>
<tr>
<td>85-24 Wr Bi Mu</td>
<td>440±5</td>
<td>465±9</td>
</tr>
<tr>
<td>85-25 Mu</td>
<td>472±9</td>
<td></td>
</tr>
<tr>
<td>85-23 Wr Bi Mu</td>
<td>441±5</td>
<td>524±5</td>
</tr>
</tbody>
</table>
is noticeably older than the other Rb-Sr phengite ages, must therefore be deemed acceptable, and included in any interpretation.

In the north of the area, the Rb-Sr phengite ages therefore define an array of values, despite the absence of significant secondary metamorphism and deformation in this area, and despite the absence of crenulation of the fabrics of the samples dated.

The K-Ar phengite ages, and most of the biotite ages are more restricted, ranging between 465 and 475 Ma and between 435 and 445 Ma old respectively. However, the K-Ar phengite ages do become younger across the Tarbert Monoform to the south-east, being as young as 443 Ma old. Thus, in general, the oldest ages are found in Central Knapdale, while younger ages occur to the north-west and to the south-east. As expected, younger ages are found to the south-east in areas that have undergone increased secondary deformation and metamorphism. However, younger Rb-Sr ages are also found to the north-west, in the biotite zone despite the lack of secondary deformation and metamorphism in this area.

The above is simply a list of the observations made concerning the whole set of geochronological data from the South West Highlands. This data set will now be discussed in more detail, for each of the two contrasting areas in the study area.

6.3.2 Knapdale and Tayvallich:

6.3.2.1 Rb-Sr Ages of Phengites:

The phengite ages show an array between 460 and 524 Ma old, generally being younger in the biotite zone, at between 460 and 505 ±5 Ma old, and older in the garnet zone, at between 490 and 524 ±5 Ma old. Sample 85-10, from the garnet isograd, gives 490 Ma, while JM2, from Tayvallich, gives 474 Ma; both these samples have very weak fractionation in Rb and Sr between the phengite and whole-rock, so the errors on these data are large. In contrast, 85-23, from Central-South Knapdale, and giving 524±5 Ma, has

\[
(\frac{^{87}\text{Rb}}{^{86}\text{Sr}})_{\text{pheng}} - (\frac{^{87}\text{Rb}}{^{86}\text{Sr}})_{\text{WR}} < 4.2
\]

so this age must therefore be accounted for in the interpretation.
Texturally, all the samples from which Rb-Sr phengite ages were derived, except 69-217 and JM2, are micaceous semi-pelites. However, 85-23 is distinctively more quartz-rich and phengite-poor than the other samples. The phengite grains are also isolated, while the phengites in the other dated assemblages are usually in mutual contact. 85-23 is therefore likely to be less affected by post-primary metamorphic fluid infiltration and disturbance of the Rb-Sr systems than the other assemblages analysed in this study. In addition, exchange between the phengite and the surroundings in 85-23 will be inhibited by the lower volume of the grain boundary/disordered region in comparison to the other assemblages. Thus, not only is 85-23 isotopically similar to the other samples from which Rb-Sr age data were derived, and not only is this sample strongly enough fractionated in Rb and Sr, but 85-23 has a texture that, of the samples dated, is most likely to preserve an older Rb-Sr age.

If D1-D2 deformation represents a time-marker, the age data are not consistent with the simple timing of a metamorphic event and subsequent cooling. If the age data did time such an event and were not reset or adjusted by subsequent exchange, the biotite zone would be expected to give the oldest ages, which would then young with increasing grade in the garnet zone as the crust which attained T_{max}>500°C cools through 500°C.

The Rb-Sr phengite age data show this range in values, despite there being no sign of over-printing metamorphism, or crenulation of the dated fabrics, in any of the samples analysed. These data therefore suggest that Rb-Sr systems remained disturbed to varying extents subsequent to the primary metamorphism. Dempster (1983) found similar behaviour in S1-S2 phengites in the Highland Border Downbend; these phengites had been reset by D4. As a result, the age of primary metamorphism, and D1-D2 deformation remains indeterminate, but will be no later than ca. 524 Ma ago, based on the oldest Rb-Sr age available.

6.3.2.2 K-Ar Ages in Phengites:

K-Ar ages in phengites from the garnet zone are similar to one another at 465 to 475±9 Ma. While these phengites are compositionally variable (section 3.2), this variability does not seem to have affected their cooling ages. In comparison, the two K-Ar ages from whole rocks published by Dewey and Pankhurst (1971) and
recalculated with the constants and abundances of Steiger and Jager (1976) are about 465 Ma old, in good agreement with the K-Ar analyses on phengite carried out in this study.

6.3.2.3 Rb-Sr and K-Ar Ages in Biotites:

Rb-Sr and K-Ar analyses of biotites agree with each other closely, giving ages of between 440 and 450 Ma, but with 86-2 from the biotite zone being 465 Ma. The close agreement in biotite ages from both systems is therefore consistent with both these systems having very similar closure temperatures. The biotites in the garnet zone are compositionally similar to one another and all are from garnet-absent assemblages except 84-20 which is garnet-bearing. The biotites in this sample would therefore be expected to be Fe-richer than the other biotites analysed (section 3.2). However, the biotite from 86-2 gives an older age of 465±9 Ma. The biotites in this assemblage are relatively coarse-grained and are Mg-rich in comparison to the other biotites analysed, with Mg/(Fe+Mg) ratios of about 0.55 to 0.56, in comparison to 0.35 to 0.45 in most other assemblages. The closure temperature for Ar in this biotite would therefore have been higher than for the biotites in the other assemblages.

6.3.2.4 Discussion:

To summarise, the geochronological data for Knapdale and Tayvallich indicate that tectono-metamorphic activity in the South West Highlands started before 524 Ma ago, and continued through to 440 Ma ago, when the crust throughout the region cooled through ca. 300°C.

The time at which the primary metamorphism occurred is indeterminate, from
the current data set, but is constrained to before 524 Ma ago. If the South West Highlands underwent regional metamorphism during a single burial-and-uplift cycle, and if cooling rates before 524 Ma ago were not significantly different to those after 524 Ma, one can guesstimate a time for primary metamorphism. The region cooled through 350-400° C about 60 Ma after 524 Ma ago, based on K-Ar cooling ages from phengites of about 465-475 Ma. During this time-span, the region cooled from 410-510° C in the biotite zone and 510-540° C in the garnet zone (section 5.3) to 350-400° C, giving a cooling rate of 1-3° C Ma⁻¹. At a cooling rate of 3° C Ma⁻¹, the area from which 85-23 was collected would take 10-15 Ma to cool from its peak temperature (ca. 530-540° C) to 500° C, the closure temperature for Sr in phengite. Hence, the primary metamorphism may have taken place at, or before, 540 Ma ago, if Sr exchange was not disturbed at all in 85-23. If some disturbance had occurred after cooling through 500° C, then, obviously, the primary metamorphism would have occurred earlier still.

30 Ma after cooling through 350-400° C, the region cooled through 300° C, the closure temperature for Sr and Ar diffusion in biotite. Hence cooling rates after closure of Ar diffusion in phengite were similar to those before, at about 1-2° C Ma⁻¹. These cooling rates are evidently very slow, both in comparison to other parts of the Scottish Dalradian which cooled at rates up to 25° C Ma⁻¹ (Dempster 1985), and to cooling rates in the Alps (table 6.7, Hawkesworth et al. 1975). Despite these slow cooling rates, low- to medium-grade, medium- to high-pressure assemblages have been preserved. Slow cooling and uplift was postulated by Graham (1986) who suggested that low rates of crustal heat production could result in preservation of the P-T conditions measured, despite the possible slow uplift rates. This suggestion is tested in chapter 7.

6.3.3 Tarbert and Northern Kintyre:

In contrast to the Knapdale and Tayvallich regions already discussed, the Tarbert and Northern Kintyre regions are dominated by over-printing mineral assemblages which grew during the secondary metamorphism at temperatures similar to, or possibly greater than, those of the primary metamorphism. I have already suggested that secondary metamorphism occurred during D₃ and D₄, which have been timed respectively at about 490-500 Ma and 440-460 Ma ago in Perthshire and Angus (Dempster 1985).
6.3.3.1 Rb-Sr Ages in Phengites:

All the phengites from Tarbert and Northern Kintyre, which have been analysed by the Rb-Sr method, are younger than ca. 500 Ma. The oldest, at 501±5 Ma, is sample 84-3, from west of Tarbert, while the youngest, at 447±5 Ma, is 84-8, from East Loch Tarbert. All four of the samples from Northern Kintyre give ages of between 460 and 470 Ma and are therefore significantly younger than the samples from the Tarbert area.

Sample 84-21 is a k-feldspar-bearing secondary pelite, with well-formed albite porphyroblasts, and relatively high modal biotite, from South Bay, and its Rb-Sr age is 488±10 Ma. The reproducibility in this sample is poor due to the low fractionation between the phengite and the whole rock, but the K-Ar age of 475±9 Ma is consistent with the relatively old Rb-Sr age. Thus, the time of growth of the earlier stage secondary assemblages is constrained to have been prior to ca 490 Ma. This age compares with the range in ages of the Barrovian Metamorphism, closely associated with D₃ deformation, in the Central Scottish Highlands Dalradian, of ca. 490-515 Ma, and is consistent with the suggested syn-D₃ growth of the early secondary assemblages. This age is therefore consistent with the suggestion that the Barrovian metamorphism in the Central Highlands, and the earlier stage of the Secondary Metamorphism in the South West Highlands, being equivalent tectonometamorphic events.

Of the samples analysed from Northern Kintyre, two of them, 87-10 and 87-18, are biotite-bearing, have relatively uncrenulated fabrics, and are therefore inferred to be primary assemblages. The other two assemblages, 85-5 and 85-6, are chlorite-bearing, biotite-free assemblages, with strongly recrystallised and crenulated fabrics. The similarity in ages of 460 to 465 Ma from all these samples is due either to the rocks’ cooling through 500°C at this time, or the young ages could be due to disturbance of the Sr systems by D₄ deformation, which resulted in the Tarbert Monoform and Cowal Antiform, though few penetrative D₄ fabrics have grown in these rocks. Dempster (1984) showed that D₄ deformation resulted in lowering of Rb-Sr ages in phengites, even when the fabrics were relatively undisturbed, so neither of the two possibilities - later cooling through 500 °C, or D₄ related disturbance of the Sr systems - can be ruled out at present, and both may have occurred.
Fig. 6.8 Across-strike transect for South Knapdale and Northern Kintyre with geochronological data:

- Rb-Sr phengite
- K-Ar phengite
- Rb-Sr biotite
- K-Ar biotite

Age (Ma) vs. Location:
- South Knapdale
- Tarbert
- Northern Kintyre
Table 6.5 Summary table of isotopic data for Tarbert and Northern Kintyre: full data listings are given in appendix I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb-Sr age</th>
<th>K-Ar age</th>
</tr>
</thead>
<tbody>
<tr>
<td>84-26</td>
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</tr>
<tr>
<td>Bi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84-3</td>
<td>501±5</td>
<td></td>
</tr>
<tr>
<td>Wr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84-21</td>
<td>477±5</td>
<td>474±9</td>
</tr>
<tr>
<td>Wr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mu</td>
<td>488±15</td>
<td>470±9</td>
</tr>
<tr>
<td>84-20</td>
<td>442±5</td>
<td>452±9</td>
</tr>
<tr>
<td>Wr</td>
<td></td>
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</tr>
<tr>
<td>Bi</td>
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</tr>
<tr>
<td>Mu</td>
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<tr>
<td>84-8</td>
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</tr>
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<td>45±9</td>
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<td>Mu</td>
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<td>87-18</td>
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</tr>
<tr>
<td>Mu</td>
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</tr>
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</table>
6.3.3.2 K-Ar Ages in Phengites:

The K-Ar ages in phengites from Northern Kintyre and Tarbert range between 475 and 440 Ma old, and tend to young towards the south-east. The oldest K-Ar age is from 84-21, at 475 Ma old. This age is therefore consistent with the 488±10 Ma Rb-Sr age for the phengite in this sample. Sample 86-3, from Claonaig at the southern end of this transect has an age of 443±9 Ma. This age is similar to the youngest K-Ar phengite ages from Tarbert and has two possible explanations. Either the effective diffusion distance for Ar in this sample has been lowered by its small grain size, or the age continues the younging trend into Northern Kintyre from Tarbert already noted. Either one, or both, of these explanations may be correct.

6.3.3.3 Rb-Sr and K-Ar Ages in Biotites:

The three biotites analysed give a much wider spread in ages than those in Knapdale and Tayvallich, ranging in age between 416±5 Ma and 477±5 Ma. The biotite from 86-8 has an Rb-Sr age of 416±5 Ma, and is therefore significantly younger than the biotites in Knapdale and Tayvallich, which vary between 438 and 442 Ma old, while 84-9 has a K-Ar age of 435±9 Ma.

The other Rb-Sr biotite age from Tarbert is from 84-21, whose phengite gave ages of 488±10 Ma (Rb-Sr) and 475±9 Ma (K-Ar). This biotite gives an Rb-Sr age of 477±5 Ma, which is substantially older than any other biotite dated in this study. The two most abundant Sr-bearing phases in this assemblage are albite and phengite; these phases probably make up about 75% of the mode of this rock (see also 4.2). Both these phases are known to have higher closure temperatures for Sr diffusion than biotite, the closure temperature for albite possibly being higher than 500°C (Giletti 1988, pers. comm. and unpubl., table 6.8). As will be discussed in 6.3.4, the exchange of Sr in lower closure temperature phases in such an assemblage, as it cools, will be inhibited as the higher closure temperature phases become closed to Sr diffusion. This is because the lower closure temperature phase, in this case biotite, will have little with which to exchange Sr. In contrast, most of the other assemblages dated in this study have relatively low modes of phengite and albite; biotite can therefore continue to exchange with a large volume of the whole-rock once phengite and albite have closed. As a result, the old biotite age in sample 84-21 is consistent, both with early closure of Sr exchange in this assemblage, and with the growth of this assemblage before D4 as argued in section 4.2. It is therefore likely that the early stages of secondary metamorphism occurred earlier than ca. 490 Ma ago.
6.3.3.4 Conclusions:

The Rb-Sr and K-Ar age data from phengites become younger from the north-west to the south-east, as the Tarbert Monoform is crossed, and as deeper structural levels become exposed. This younging therefore correlates with increasing metamorphic grade (chapter 3), exposed structural depth, and extent of secondary deformation and metamorphism, and would have been due to some combination of some, or all of these factors. Essentially, rock initially buried deeper would have reached higher initial temperatures, and may have taken longer to cool through a given temperature. Alternatively, the geochronometer systems may have been disturbed further by increased secondary deformation. Neither of these two alternatives can be ruled out at the moment, and both were probably important.

The age data from Tarbert and Northern Kintyre are also consistent with the syn-D₃ timing of growth of the earlier secondary assemblages argued for in section 4.2, since phengites that grew after albite porphyroblasts give an Rb-Sr age of 488±10 Ma.

6.3.4 "Inconsistent" Ages; Exchange Reservoirs and Their Isotopic Variation:

It is difficult to objectively decide on the consistency of a given geochronological data set, and often, this decision can only be made on criteria of internal consistency (section 1.1 and references therein, 6.3.2). Most of the data presented here define clear patterns, with most Rb-Sr phengite ages lying between 460 and 525 Ma old, while most Rb-Sr ages in biotites fall between 435 and 445 Ma old. However, several samples analysed in this study give ages that are internally inconsistent, both with the patterns just summarised, and with external time constraints on Dalradian metamorphism.

Most of the inconsistencies were from the Rb-Sr method applied to phengite. While the analytical errors associated with Rb-Sr dating are smaller than those associated with the K-Ar method, problems usually arise with correction for initial radiogenic $^{87}$Sr in the sample. This correction is normally made by analysing the whole-rock, assumed to represent the large exchange reservoir. The K-Ar method relies on the assumption of no radiogenic $^{40}$Ar at $t = 0$; violation of this assumption is relatively easily recognised as an anomalously old age and can be tested for independently by the Ar-Ar method if necessary. Violation of the assumption that the whole-rock represents the Sr exchange reservoir is also
recognised by anomalous ages (e.g. Dempster 1986), but independent testing of this assumption is much more difficult, since this testing needs the replacement of one invoked and assumed initial Sr ratio with another, otherwise an age cannot be calculated. Besides which, an anomalous age can often only be recognised by comparison with other ages taken to be consistent, thus begging the question two times over. The other assumption that needs to be made with the Rb-Sr method is that the exchange reservoir, represented by the whole-rock, does not change composition significantly during the rock’s cooling history.

Some of the samples which show internal inconsistency will now be discussed, and it will be shown that, while some of the inconsistencies are due to artifacts of the age calculation methods, specifically of the problem of correcting for initial radiogenic $^{87}$Sr, other inconsistencies are due to the assemblages with which the sample concerned co-exists.

The changing isotopic composition of minerals in a rock over time can be represented on diagrams such as those in Figs 6.9 to 6.11. These are of rocks in which we shall [three Rb and Sr-bearing phases: phengite, albite, and biotite. By observation in this and other studies, the Rb/Sr ratios in these phases obey the following relationship:

$$ (Rb/Sr)_{bi} > (Rb/Sr)_{pheng} > (Rb/Sr)_{ab} $$

In addition, closure temperatures for Sr diffusion in albite, from initial, unpublished diffusion data (Giletti 1988, pers. comm.) are about 500 to 550 °C, depending on effective diffusion distances and cooling rates (table 6.8) Thus, I assume that albite is the first of the phases being considered to close, though its closure temperature may be similar to that of phengite, and some studies (e.g. Dempster 1986) indicate that plagioclase closes later than phengite. The major difference between the pelitic assemblages in the South West Highlands and similar assemblages in other metamorphic belts is that the plagioclase is close to pure albite, and is therefore less likely to have diffusion distances lowered by sub grain boundaries etc, and be less reactive, than more anorthitic feldspar more normally found in other metamorphic belts.

Fig 6.9 is the isotope evolution diagram for an assemblage which crystallises at time $t_1$, at or below the closure temperature for albite, but above the closure temperature for phengite. This model assemblage would therefore be similar to the garnet zone pelites of Knapdale. This diagram would also be applicable to the isotopic evolution of phengites in the Northern Kintyre assemblages. As a result of the closure of the albite, phengites do not exchange with a reservoir whose
Table 6.6: Closure temperature calculations for Sr in phengite: these calculations make a number of assumptions: see text for details.

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Closure temperature (±5°C)</th>
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</thead>
<tbody>
<tr>
<td>$D_0 = 0.6 \text{ cm}^2 \text{ Ma}^{-1}$, effective distance 0.01 cm:</td>
<td></td>
</tr>
<tr>
<td>$1^\circ \text{C Ma}^{-1}$</td>
<td>400</td>
</tr>
<tr>
<td>$3^\circ \text{C Ma}^{-1}$</td>
<td>445</td>
</tr>
<tr>
<td>$10^\circ \text{C Ma}^{-1}$</td>
<td>500</td>
</tr>
</tbody>
</table>

| Effective distance 0.005 cm: | |
| $1^\circ \text{C Ma}^{-1}$ | 350 |
| $10^\circ \text{C Ma}^{-1}$ | 425 |

| $D_0 = 0.06 \text{ cm}^2 \text{ Ma}^{-1}$, effective distance 0.01 cm: | |
| $1^\circ \text{C Ma}^{-1}$ | 500 |
| $10^\circ \text{C Ma}^{-1}$ | 625 |

Table 6.8: Closure temperature calculations for Sr diffusion in albite and orthoclase, using unpublished diffusion parameters from B. Giletti (pers. comm.):

**Albite:** $(D_0 = 0.014 \text{ cm}^2 \text{ s}^{-1}, Q = 54 \text{ kcal mol}^{-1})$

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Closure temperature (±5°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^\circ \text{C Ma}^{-1}$</td>
<td>490</td>
</tr>
<tr>
<td>$10^\circ \text{C Ma}^{-1}$</td>
<td>527</td>
</tr>
</tbody>
</table>

**Orthoclase:** $(D_0 = 3.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}, Q = 42 \text{ kcal mol}^{-1})$

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Closure temperature (±5°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^\circ \text{C Ma}^{-1}$</td>
<td>498</td>
</tr>
<tr>
<td>$10^\circ \text{C Ma}^{-1}$</td>
<td>543</td>
</tr>
</tbody>
</table>
Table 6.7: Comparative cooling rates between the South West Highlands and the areas in the Central Highlands for which detailed constraints are available:

### South West Highlands

Cooling Rates (°C Ma⁻¹):

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>Biotite zone</th>
<th>Garnet zone</th>
<th>Northern Kintyre</th>
</tr>
</thead>
<tbody>
<tr>
<td>530-500</td>
<td>1-2</td>
<td>&lt;3</td>
<td>Heating?</td>
</tr>
<tr>
<td>500-470</td>
<td>1-2</td>
<td>3-5</td>
<td>3-5</td>
</tr>
<tr>
<td>470-440</td>
<td>1-2</td>
<td>1-2</td>
<td>3-5</td>
</tr>
</tbody>
</table>

### Central and Southern Highlands:

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>North Angus</th>
<th>Central Angus</th>
<th>North Perthshire</th>
<th>South Perthshire</th>
</tr>
</thead>
<tbody>
<tr>
<td>530-500</td>
<td>15-25</td>
<td>3-5</td>
<td>1-3</td>
<td>1-2</td>
</tr>
<tr>
<td>500-470</td>
<td>4-5</td>
<td>3-5</td>
<td>1-3</td>
<td>1-2</td>
</tr>
<tr>
<td>470-440</td>
<td>4-5</td>
<td>15-20</td>
<td>15-20</td>
<td>1-2</td>
</tr>
</tbody>
</table>

South West Highlands cooling rates from this study, Central and Southern Highlands cooling rates from Dempster (1985):
Fig. 6.9 Sr-isotope evolution diagram for an albite-phengite-biotite-bearing assemblage petrologically and isotopically equilibrated at, or below, the closure temperature for Sr diffusion in albite (see text for discussion):
composition is given by the whole-rock (WR on the figure), but with a more Rb-rich and radiogenic reservoir, R-1, which evolves isotopically through time along the extension of the albite-whole rock tie line. This tie line is in fact an isochron, which gives the growth age of the assemblage. Phengite closes at a later time t-2, the time since t-2 being given by the phengite-R-1 isochron. Obviously, in a rock where the mode of albite is low, R-1 and WR will be close to being coincident, and the phengite-WR isochron age will be close to the true cooling age of the phengite. If there is strong fractionation of Rb and Sr between the whole rock and phengite, the phengite-WR isochron will be close to the phengite-R\textsubscript{1} isochron, but will always have a greater slope. Phengite - whole rock ages are therefore always maximum age estimates.

Fig. 6.9 assumes that albite is the first phase in the hypothetical assemblage to close to Sr diffusion during cooling. If phengite actually closed first, or if albite is absent, a phengite - whole-rock isochron will obviously give a correct age (see Fig. 6.10). Thus, the Knapdale garnet zone ages from phengites are likely to be closer approximations to the true cooling ages than the age from the albite porphyroblast-bearing assemblage, 86-4 (6.3.3). The age from this assemblage is the oldest of the Northern Kintyre samples, consistent with the prediction of Fig. 6.10.

On the closure of the phengite in Fig. 6.9, biotite now exchanges with a reservoir, whose composition, less radiogenic than that of the whole rock, is given by R\textsubscript{2}. Since this reservoir must also lie on the albite-WR isochron, the biotite is initially less radiogenic than the whole rock; its \( \frac{87}{86} \text{Sr} \) ratio at time \( t_2 \) is given by Bi-\( t_{2a} \). At time \( t_3 \), the albite-WR tie-line has evolved to Ab-\( t_3 \) - WR-\( t_3 \) making the biotite more radiogenic. The biotite closes at time \( t_3 \), then evolves further. Since biotite is usually very Rb-rich, the \( \frac{87}{86} \text{Sr} \) ratio changes rapidly. With the usual (mineral-whole rock) age calculation method, biotite cooling ages are given by Bi-\( t_4 \) - WR; this is a minimum estimate and the real cooling age is given by Bi-\( t_4 \) - R\textsubscript{2}-\( t_4 \). Where the fractionation of Rb and Sr between biotite and whole rock is strong, the errors associated with the age calculation method used here are not significant. However, where this fractionation is weak, the errors become significant, and the calculated age of the biotite is anomalously young. In such cases, the assumption that the exchange reservoir does not change composition significantly has been violated by the earlier closure of high closure temperature and less radiogenic phases.

In this study, two biotite age data which illustrate this problem were obtained. They are samples 84-8 and 84-3 giving biotite ages of 429±5 and 220±5 Ma.
Fig. 6.10 Sr-isotope evolution diagram for an albite-absent assemblage equilibrated above the closure temperature for Sr diffusion in phengite (see text for discussion):
respectively (see appendix, p.436). Both these samples are green biotite-bearing secondary pelites and are relatively quartzitic. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in both these biotites are low relative to those in older biotites, at less than 1.0, and the younger of these two samples, 84-3, has the least radiogenic biotite, $^{87}\text{Sr}/^{86}\text{Sr}$ being at 0.7887. Both these samples also have relatively radiogenic phengites; the closure of these at higher temperatures would have resulted in $R_2\cdot t_4$ (Fig. 6.9) in both these rocks having compositions significantly different to those of the whole rock analyses. The composition of $R_2\cdot t_4$ in any given rock is likely to be indeterminate unless all minerals in the rock are analysed and a detailed modal analysis of the assemblage made.

Figs 6.9 and 6.10 describe the isotopic evolution of assemblages in which significant exchange of Sr between biotite and other phases, and the grain boundary region of the rock, occurs once Sr diffusion in phengite and albite has closed. However, some of the South West Highlands assemblages are very albite- and phengite-rich, these assemblages being the k-feldspar bearing albite porphyroblast schists from South Bay (4.2, 4.4.4). An Rb-Sr biotite age from one of these assemblages, 84-21, was about 35 Ma older, at 477±5 Ma old, than any other Rb-Sr biotite age derived in this study (6.3.3.3). The isotopic evolution of a cooling assemblage like 84-21 is now considered (Fig. 6.11).

If significant exchange of Sr between the grain boundary and biotite does occur once all volume diffusion of Sr, except in biotite, has ceased, the reservoir with which such exchange occurs will be given by $R_1$ on Fig. 6.11 while biotite has the composition $\text{Bi-t}_2(2)$. In the cooling assemblage considered in the figure, all volume diffusion, except for in biotite, ceases at time $t_2$, and $R_1$ has the composition $R_1\cdot t_2$. On closure of the biotite at time $t_3$, the mineral - whole-rock cooling age is given by $\text{Bi-t}_3(2) - \text{WR-t}_3$ while the correct cooling age is indeterminate and given by $R_1\cdot t_3 - \text{Bi-t}_3(2)$. Thus, if much exchange of Sr between the biotite and the grain boundary occurs once the phengite and albite are closed, the biotite - whole-rock cooling age will be a minimum age, while if very little, or no, exchange occurs between biotite and the grain boundary region, the biotite - whole-rock age will be accurate, and close to the phengite age in the same sample.

Fig. 6.11 therefore shows how biotite and phengite Rb-Sr ages from a single sample may coincide, the biotite being anomalously old compared with other biotite Rb-Sr ages in the same metamorphic belt. 84-21 confirms the predictions made in Fig. 6.11; if the mineral ages from 84-21 have a coherent, rational explanation, the exchange of Sr between the biotite and the surroundings must

0 0 3 2 3
Fig. 6.11 Sr-isotope evolution diagram for an assemblage made up only of albite, phengite and biotite and re-equilibrated at, or below, the closure temperature for Sr in phengite (see text for discussion):
have been inhibited once phengite and albite had closed to Sr diffusion. This is an important conclusion, since it allows the interpretation of the 488 Ma ages in terms of growth of the albite porphyroblasts at, or before, this time. Hence, these age data are consistent with the syn-D\textsubscript{3} growth timing of these assemblages.

Concluding this subsection, the isotopic evolution diagrams suggest that, assuming that albite has a higher closure temperature for Sr diffusion than phengite, correcting for initial \textsuperscript{87}Sr with a whole-rock analysis will give errors which will become significant if the fractionation of Rb and Sr between the mineral and whole-rock is weak. Since phengites tend to close early, the difference between the whole-rock composition and that of the reservoir with which phengite actually exchanges will not be large. However, the exchange reservoir for biotite, once other phases in the rock have closed, may be significantly different to that of the whole-rock. Fortuitously, biotite is often extremely radiogenic, so these differences do not usually alter the resulting age significantly (e.g. Cliff et al. 1985).

In the absence of diffusion data for Sr in phengite, the only available constraint on the closure temperature is the empirical study of Purdy and Jager (1975; see also 6.2.2). How the closure temperature changes with effective diffusion distance and cooling rate cannot be assessed, but these changes may be large (table 6.6, 6.4.2). However, in Purdy and Jager (1975), the actual value of the closure temperature would not be affected by the assumptions in the method of age calculation because that study shows that ages are reset by re-heating above a certain metamorphic grade; the temperature of resetting would be determined, though the time of resetting may not be.

6.4 Conclusions and Implications:

This chapter was designed to fulfill two roles. One was a theoretical discussion of the closure temperature concept, and of the methods used to calculate ages from mineral analyses, while the other role was the presentation of the radiometric age data gathered in this study. Since conclusions have already been drawn for the theoretical components of this chapter, this section is designed to conclude the geochronological data and to assess its implications in the light of the conclusions drawn and the conjectures made in previous chapters, and the contribution of the geochronological studies towards the fulfilment of the main
aim of this study, to construct integrated P-T-t histories for the Dalradian of the South West Highlands.

The conclusions drawn in the previous chapters concerning the thermal history of the South West Highlands can be summarised in the suggestion that regionally-developed high-pressure low- to medium-temperature assemblages have been preserved in a metamorphic belt characterised by long periods of time spent at temperatures close to the highest preserved in the assemblages now present. The evidence for protracted high temperatures lies mainly in chemical disequilibrium in phengites and the partial resetting of garnet growth zoning. As a result of the disequilibrium in the phengites, the Sr systems in the samples analysed may have been disturbed to some extent after the growth of the mineral fabrics that are been dated, even if there is little evidence in the textures for re-activation or recrystallisation of these fabrics. As a result, the age data cannot be taken at face value, but need to be interpreted with care bearing in mind the possibilities for such resetting.

The age data give constraints on the timing of the metamorphic episodes that occurred in the South West Highlands, as well as assessing the rates of cooling after the attainment of peak temperatures. The cooling rates can be calculated from the closure temperature estimates made in section 6.3, and the geothermometry estimates made in chapter 5, for the primary and secondary metamorphic episodes. From the cooling rate data, the uplift rates of the area can be calculated, by use of the pressure estimates of primary and secondary metamorphism. By the addition of absolute time measurements, the constraints on the thermal history of the crust during burial and uplift are made much stronger, as was discussed in chapter 1. The thermal models to be discussed in chapter 7 are therefore better constrained, and their ability to predict the thermal controls of regional metamorphism is improved as a result.

6.4.1 Primary Regional Metamorphism:

In this discussion, it should be remembered that a mineral age can be reset or disturbed after growth of the mineral being dated, either by heating to high enough temperatures for long enough to allow significant exchange of the radiogenic species by diffusion, or by recrystallisation of the phase at lower temperatures than the closure temperature for the diffusion. Both these
alternative ways of resetting a mineral age can lead to partially reset "mixed" ages, and they are not mutually exclusive. A mineral grain can also take part in exchange reactions with the other phases in the assemblage even in the absence of deformation, and such exchange may lead to exchange of, for example, Rb and Sr, leading to the resetting of ages. If these processes have occurred in a sample in the absence of deformation, they will probably be sluggish, leading to scatter in analytical results. As a result, sampling bias may occur, and may give rise to misleading results.

It was suggested in chapter 5 that sluggish kinetics for resetting of phengite chemistries by the TS exchange may have occurred as a result of high temperatures being maintained for long periods after primary metamorphism, resulting in increasing disequilibrium in phengite analyses from lower grade to higher grade samples. It was also suggested that probe data from a given sample may preferentially sample part of the range in phengite chemistry present in the assemblage. Similar sampling bias problems may be associated with the isotopic analyses, since the separation techniques (see appendix) tend to sample the magnetic fractions of phengite preferentially. The magnetic fractions are Fe-rich, hence celadonite-rich, and may therefore represent the earlier-formed phengite. In the absence of information on Sr distribution within original grains, this possibility is untested at present, but it may be that at least some of the scatter in Rb-Sr ages is due to sampling bias. If this is so, it implies that the kinetics of the resetting of Sr systems by mineral reaction and exchange in the absence of deformation may also be sluggish, though clearly at temperatures above the closure temperature for Sr diffusion, such reaction-related resetting will no longer be rate-limiting.

All the cooling age data from Tarbert and Northern Kintyre suggest that the latter area cooled through given temperatures later than Knapdale and Tayvallich. Though the peak temperatures in Northern Kintyre are unknown, due to the absence of Barrovian assemblages, these were probably higher than those in Knapdale since the crust was at deeper structural levels and is free from mafic rock (section 3.6). Thus, it is even more likely that the factors causing disturbance of the Sr systems were influential in Northern Kintyre, especially with the pervasive secondary deformation.

All the above speculations leave open the question of the scattering of ages in the biotite zone, the part of the region which experienced the lowest temperatures,
but which also has relatively young ages despite little evidence of overprinting
deformation and metamorphism. In sections 3.4 and 3.5, it was shown that the
actinolite-to-hornblende isograd had been folded by tightening centred on the
Loch Awe Syncline. If deformation can enhance the kinetics of the disturbance of
Sr systems without causing significant crenulation or recrystallisation of the
phengite fabrics, as found by Dempster (1984), similar processes in the biotite
zone might explain why the resetting of Sr systems in lower grade rocks was
apparently more enhanced than in higher grade rocks, especially if much of the
tightening on the Loch Awe Syncline occurred during D₄ deformation. As a
result, even slight deformation may enhance greatly the kinetics of resetting of Sr
systems in phengites.

By the time of D₄ deformation, at 440 to 450 Ma, the region had cooled below
c. 350-400°C, since K-Ar cooling ages from phengites are nearly all between 465
and 475 Ma old. Depending on the difference between the clapeyron slopes of
phengite chemistry and the slope of the P-T-t path during D₄ deformation, it is
possible that the cooling would tend to make the phengites more celadonite-rich,
hence more magnetic (see also Fig. 5.14). As a result, the separation techniques
would tend to sample preferentially the younger phengites, in contrast to what
might have happened during preparation of samples from garnet zone assemblages
in which the magnetic phengites would tend to be older. There are therefore two
possible explanations for the younger biotite zone ages; these are: sampling bias,
and the enhancement of kinetics of resetting by the presence of suitable phases
co-existing with the phengite and by deformation. These two alternatives are not
mutually exclusive.

Much of this discussion of the age data has been necessarily speculative and
unconstrained by facts, but it seems difficult to reconcile the geochronological
data, which shows much scatter, with the probability that the fabrics concerned
formed over a short time interval with little diachroneity. The reasons for having
confidence in this speculation are that petrological and textural information
indicate that the rocks probably remained at high temperatures for a long time
after the primary metamorphism. Thus, the scatter of the age data is probably due
to Sr systems in phengites remaining open after the primary metamorphism,
probably as a result of chemical resetting in the absence of significant
re-crystallisation, but enhanced in some cases by non-pervasive strain and
deformation in some parts of the crust.
6.4.2 Secondary Metamorphism:

The secondary metamorphism occurred at, or earlier than, 488 Ma, based on the oldest Rb-Sr cooling ages for phengites from secondary assemblages. This timing is consistent with the suggestion made in chapter 4 that the textures of the secondary metamorphic assemblages are more consistent with a syn-D₃ timing than a syn-D₄ timing for this event. Since the crucial age dates were gathered from fabric-forming minerals, the absence of penetrative D₄ crenulation cleavages, noted in chapter 4, is the main reason for the absence of D₄ mineral ages in the South West Highlands.

The young, but uniform, ages from assemblages from Northern Kintyre suggest that this area remained at high temperatures for longer than Knapdale and Tayvallich, though deformation-enhanced resetting of Sr systems may have also occurred as a result of D₄ deformation. Ages from the lower closure temperature systems are also lowered as the Tarbert Monoform fold axis is crossed. These ages indicate that the Northern Kintyre rocks cooled through given temperatures about 30 Ma later than in Knapdale and Tayvallich throughout their cooling history. Though the peak metamorphic temperatures and their times of attainment are unconstrained in Northern Kintyre, the geochronological data, and the P-T data in chapter 5, all suggest that the peak temperatures in Northern Kintyre were higher than those in Knapdale.

Further constraints on these speculations would be provided if order-of-magnitude calculation of the variation of the closure temperature of Sr in phengite with cooling rates could be made. Strictly, this would not be possible, since diffusion parameters for Sr in phengite are not available. However, biotite and phengite are almost identical structurally, and unpublished initial Sr diffusion data for biotite suggest that the activation energy for Sr diffusion is similar to that for Rb, at 21 kcal mol⁻¹ (Hofmann and Giletti 1971, Giletti 1988 pers. comm.). Because of the close similarity in crystal structure between phengite and biotite, it might be reasonable to suggest that the activation energies for Sr in both phases are similar, the differing closure temperatures resulting from differing D₀ values.

Thus, calculations have been made using the expression of Dodson (1979). Firstly, a closure temperature for Sr of 500°C, an activation energy of 21 kcal mol⁻¹, cooling rates of 1 and 10°C per Ma, and an effective diffusion distance of
0.1 cm were used to calculate $D_0$ values (table 6.6). The two $D_0$ values resulting were then used to calculate closure temperatures for the hypothetical diffusing species. The aims of this calculation were therefore to examine possibilities; it is not intended to suggest that the values resulting are the closure temperatures for Sr in phengite under the conditions concerned, rather, it is the aim to evaluate the effect of varying cooling rates on the possible resetting of Sr systems in phengites. The diffusion of Sr in biotite has a relatively low activation energy (cf table 6.2), so the effect on closure temperatures of varying grain sizes and cooling rates may be larger than that for other systems.

The results of the calculations are shown on table 6.6. For 1°C per Ma cooling rates, the hypothetical closure temperature is at least 100°C lower than that for 10°C per Ma cooling rates, for both values of $D_0$. The differences in closure temperatures between cooling rates of 1 and 3°C per Ma are about 45 to 50°C.

The phengites in the biotite zone samples are finer grained than those in the garnet zone, so the effect on closure temperatures of variations in the effective diffusion distances was also examined. Halving the effective distance resulted in a lowering of closure temperatures of about 50 to 70°C for a given cooling rate.

Thus, if the hypothetical mineral-diffusing species system is an accurate reflection of the diffusion of Sr in phengite, it is possible for the differences in cooling rate and grain size alone between the biotite zone and garnet zone samples to account for much of the variation in ages, with an implied closure temperature difference of up to 100°C. Add to this the possible late tightening on the Loch Awe Syncline already postulated, and the younging of the biotite zone phengite ages is less surprising than it first appeared.

6.4.3 Uplift and Cooling Rates:

Thermal models of regional metamorphism show that the facies series preserved in a metamorphic belt often depends on uplift and cooling rates, all other thermal properties being equal (see also section 7.3). As a result, the most important aim of this chapter is to constrain uplift and cooling rates from the geochronological data, and from the P-T conditions of metamorphism preserved in the assemblages formed over time and derived in chapter 5. The reasons for this are two-fold: to test the suggestions of high temperatures being maintained for
long periods of time that have already been made several times in this thesis, and to constrain the thermal models to be made in chapter 7 with quantitative time estimates of regional metamorphic processes in the South West Highlands. Obviously, the interpretation of the geochronological data has been complicated by several factors, some of which have been discussed above, and most of which are not well constrained at present, but, it is still possible to make estimates of uplift and cooling rates from the P-T-t data available. The values of the cooling and uplift rates will obviously be time-integrated averages between the time data points available (e.g., between Rb-Sr and K-Ar ages in phengites). Uplift rates for the South West Highlands are shown on table 6.7.

The time of attainment of syn-D1-D2 temperatures was probably about 525 Ma ago, based on the oldest Rb-Sr phengite age, and Knapdale cooled through 350-400° C (from K-Ar cooling ages on phengites) about 475 Ma ago, and through 300° C (biotite ages) about 440 Ma ago.

The pressures of primary metamorphism were 9-10 kbar in Tayvallich, 10-11 kbar in South Knapdale, and 11-12 kbar in Northern Kintyre (section 5.3). This corresponds to depths of about 32 to 35 km, 35 to 38 km, and 38 to 40 km, depending on the densities of the crust that rested on top of the rock now on the surface, taken to be 2.8 to 3.0 g cm⁻³. P-T conditions after the primary metamorphism are best constrained in South Knapdale, hence uplift rates for this area will be worked out first, followed by uplift rates for Tayvallich and Northern Kintyre, which are dominated by one set of assemblages, these having formed at different stages in the P-T-t history of the South West Highlands.

In South Knapdale, the estimated pressures of the earlier stages of the secondary metamorphism are ca. 8 kbar, corresponding to depths of 24 to 28 km, using the same density range as before. The earlier stages of secondary metamorphism occurred at about 500 Ma ago, so about 10 km of uplift occurred in about 25 Ma, translating to uplift rates of about 0.4 km per Ma. Due to the errors on pressure estimates, and on the timing of attainment of the respective pressure conditions, this uplift rate could vary by up to 0.2 km per Ma.

The later stages of the secondary metamorphism, which occurred at temperatures of about 300 to 350° C, the lower temperature stability limit of biotite in k-feldspar-bearing assemblages (section 5.4), is inferred to have occurred at about 440 to 460 Ma, the range in biotite cooling ages. Pressure
conditions were about 6 Kbar, translating to depths of 19 to 21 Km. Thus about 5 to 7 Km of uplift occurred in 40 to 60 Ma, at rates of about 0.1 to 0.2 km per Ma.

As has been said, these uplift rates are approximate, but it is likely that they were quicker prior to $D_3$ deformation than after this event, suggesting that uplift rates may have decayed exponentially (see England and Richardson 1977). However, any rapid or pulsed uplift that may have occurred as a result of large scale deformation is undetectable by the information available at present.

The probability that $D_1$-$D_2$ fabrics formed more-or-less simultaneously throughout the region, coupled with the similarities in K-Ar phengite cooling ages indicates that the biotite zone cooled much more slowly than the garnet zone. This supposition is consistent with the garnet zone being initially at greater depths than the biotite zone, and the formation of the Knapdale Steep Belt and tightening of the Loch Awe Syncline, which probably occurred during $D_4$ deformation (section 2.2, and 6.3); the garnet zone needs to have "caught up" the biotite zone at some stage in its uplift history, and this would have occurred during the formation of the Knapdale Steep Belt. If the biotite zone was at depths of 32 to 35 km during the primary metamorphism, at 525 Ma, and depths of 16 to 20 km at 440 Ma, the resulting uplift rates would be about 0.15 to 0.2 km per Ma.

Uplift rates in Northern Kintyre were probably similar to those in Knapdale, because of the possibility that cooling through given temperatures seems to have occurred about 20 to 30 Ma later than in Knapdale. This observation precludes uplift rates being significantly quicker than in Knapdale, and may mean that they were slower. The later cooling of Northern Kintyre may be due to the Cowal Flat Belt's remaining flat while the Knapdale Steep Belt was forming, presumably after 500 Ma. Due to lack of knowledge, uplift at the same rates as were derived for South Knapdale, 0.3 to 0.4 Km per Ma prior to 500 Ma, and 0.15 to 0.2 Ma after 500 Ma will be assumed to have occurred.

The cooling rates just calculated from the geochronological data, of ca 1 to 3 °C per Ma, are similar to the estimates made for the cooling rates necessary to reset garnet zoning in sample 86-8 (sections 3.3, 5.4). These cooling rates are also substantially slower than those measured in the alps, of ca 20° C (eg Hawkesworth et al. 1975, Dodson 1979), and those measured in other parts of the Scottish Dalradian, which were variable but ranged between 5 and 25°C per Ma (Dempster 1985) The variation in cooling rates between the South West Highlands
and other parts of the Dalradian are summarised in table 6.7. Thus, as postulated by Graham (1986), the uplift and cooling rates in the South West Highlands after the primary metamorphism were very slow, thus making the preservation of high-pressure, low-temperature assemblages all the more remarkable. In addition, while cooling rates in the Perthshire and Angus Dalradian were variable over the period of uplift, there is no evidence for variability of such magnitude in the South West Highlands, either over time or along or across-strike. The only variability appears to have been that the biotite zone uplifted even more slowly than the garnet zone. This variation is in itself remarkable since the most "blue-schist-like" area in the region has experienced the most un-blueschist-like cooling and uplift history.

6.4.4 Implications of the Geochronological Data For the Thermal History of the Region:

The age data presented in this chapter has four major sets of implications for the P-T-t histories of the South West Highlands:

1. The attainment of peak metamorphic temperatures in a region of thickened continental crust normally takes ca 20 to 40 Ma, depending on heat production rates (eg England and Richardson 1977). This is because the length-scales of conductive heat transfer in a regional metamorphic belt are large, so that the time-scales of response of rocks to thermal disequilibria in the crust are of this order. As a result, thickening would probably have occurred by 545 Ma at the latest, hence Caledonian orogenesis would have started much earlier than is normally accepted (eg Dewey and Shackleton 1984). In addition, the time of the ending of deposition in the Dalradian, which is not well constrained (chapter 2), is likely to have been before ca. 545 Ma.

2. The cooling age data presented in this chapter, and the geothermometry presented in chapter 5, both indicate that the crust in Northern Kintyre remained at high temperatures for at least 30 Ma. Thus, Northern Kintyre underwent metamorphism at the same time as the prograde metamorphism in the Central Highlands, the contrast between the two regions in the Scottish Dalradian being that while the syn-D_3 assemblages in the Central Highlands are dominant and tend to be the first regional assemblages to be preserved, in the South West Highlands, the syn-D_3 assemblages are subsidiary, although locally pervasively developed, and overprint earlier, higher pressure assemblages that are dominant over a larger area.

3. The crust at Northern Kintyre was at elevated temperatures at the time of the early secondary metamorphism, and may have still been on the heating, rather than the cooling, phase of its P-T-t path. It is certain that the garnet zone of Knapdale cooled slowly, and may also have spent a long time at temperatures close to those of the primary metamorphism. Despite this, no
metamorphic reactions were exceeded at this time in the garnet zone, while secondary metamorphism was pervasive in Northern Kintyre. The major difference between the tectono-metamorphic histories of the two regions is the D3 deformation in Northern Kintyre, during which, the early secondary metamorphism occurred. Thus, the factor which decides whether regional metamorphism occurs or not seems to be the presence of deformation, with fluid infiltration.

4. The major thermal problem of the regional metamorphism in the South West Highlands is the preservation of regionally-developed, high-pressure low- to medium-temperature assemblages in an area that remained at high temperatures for a long period of time. Usually, much higher temperatures would be expected the 35 Km depths implicated by the pressure estimates. The controlling influences of regional metamorphism in the South West Highlands must therefore have been anomalous in comparison to most other metamorphic belts, in order to result in high pressure, low to medium temperature assemblages being developed and preserved as the dominant assemblages in the region, rather than the more usual overprinted remnants.

All these implications are to be discussed further in chapter 7, where the thermal regime (heat production and transfer rates etc.) imposed during regional metamorphism will be quantified. This will lead to a formal elucidation of the main controlling factors of regional metamorphism in the South West Highlands.
CHAPTER 7
THERMAL MODELS OF REGIONAL METAMORPHISM

"Their presence and their impatient energies, like some colossal internal combustion generator idling below so as to be always prepared for another foray into the upperworld, were there by implication in the feverish beat and urgent throbbing of that overheated earth and sky..."

Laurens van der Post, Yet Being Someone Other

The South West Highlands can be divided into two parts according to their metamorphic history: the north-west where the metamorphic history is relatively simple, and the south-east, where the metamorphic history is more complex. The dominant primary assemblages formed under P-T conditions such that the pressures were high for the temperatures attained in comparison with similar "Barrovian" metamorphic belts throughout the world, being about twice as high as would normally be expected given the assemblages that formed. The more locally developed secondary overprinting assemblages grew over a long period of time, the early stages of this growth being at similar temperatures to those under which the dominant, primary assemblages grew.

Despite the preservation of high pressure assemblages, the crust now exposed shows no signs of having cooled rapidly, rather, cooling rates were less than 5 °C per Ma throughout the metamorphic history of the area. This is in stark contrast to most thermal models of regional metamorphism already published which suggest that rapid uplift and cooling is normally required for the preservation of high-pressure, low temperature metamorphic assemblages (Fig. 7.1).

England and Thompson (1984) modelled a comprehensive series of P-T-t paths for thickened continental crust with a variety of thermal properties. Remembering that the facies series of a metamorphic belt is the locus of preserved (P-T)-S_max conditions (chapter 1) attained diachronously along a piezothermic array, these models showed that the facies series that develops in a given metamorphic belt depends critically on crustal radiogenic heat production rates, the conductivities, and the uplift and erosion rates. The preponderance of Barrovian facies series metamorphic belts throughout the world suggests that most
of the critical thermal properties just itemised are similar in magnitude, hence that preservation of non-Barrovian facies series P-T conditions over regional scales requires that the thermal properties of the crust undergoing metamorphism vary significantly from those values usually found. Thus, preservation of high temperature, low pressure (Buchan) facies series requires an enhanced heat flux (eg Wickham and Oxburgh 1987, De Yoreo et al. 1988, in press), while preservation of high pressure, low temperature facies series metamorphism requires low heat flux, or rapid uplift rates, or both (below, 7.1).

The metamorphism in the South West Highlands has resulted in the preservation of high pressure, low temperature assemblages over regional scales, as the dominant assemblages formed, in contrast with other areas in the Scottish Dalradian where the dominant assemblages tend to define a Barrovian zonal sequence, but with localised variation super-imposed. Thus, the Dalradian is divided into provinces reflecting differences in the metamorphic histories (Harte 1988), these differences in turn being due to differences in the pre-metamorphic history of the region (Harte et al. 1984, see also section 2.3 and chapter 8), and the South West Highlands being one of the larger of these provinces.

Thus, having reconstructed the P-T-t histories in the South West Highlands, it is clear that the critical properties of the crust in this region were probably unique, in that they allow the preservation of regionally developed high-pressure low temperature assemblages in a region that has uplifted slowly, and has probably remained at temperatures close to those preserved in the primary assemblages for unusually long time-scales. This chapter has the aim of finding the values of the critical thermal properties (heat production, uplift rates, and conductivities) that are necessary to reproduce the observed P-T-t histories in the region, and to show that the values of the critical properties are consistent with measured values of these properties from lithologies similar to those that are present in abundance in the South West Highlands, and are unique to this region with respect to the rest of the Scottish Dalradian.

Richardson and Powell (1976) measured heat production rates and conductivities in Dalradian lithologies, and Graham (1986) argued that, based on these measurements, the South West Highlands crust would have had low rates of heat production relative to those in most Dalradian lithologies, and the metamorphic history of the region would therefore be anomalous. This thesis has shown that the metamorphic history in the South West Highlands was indeed
Fig. 7.1 Early exhumation of blueschist facies rocks: the P-T conditions of the blueschist facies are attained early on in the history of an orogenic belt according to the models of England and Richardson (1977) and therefore tend to be exhumed earlier than the Barrovian Facies series assemblages which will tend to overprint the blueschist assemblages if uplift rates are slow. The preservation of blueschists is therefore due to a combination of early exhumation and the rapid uplift necessary to prevent thermal relaxation of the rocks to higher temperatures.
anomalous, and the models whose results are to be presented in this chapter will show that the necessary rates of heat production are consistent with the measurements of Richardson and Powell (1976).

7.1 The Preservation of Low-Temperature High-Pressure Assemblages:

Since the study of England and Richardson (1977), several studies have been made of the crust and upper mantle, involving thermal models of rocks in which blueschist facies P-T conditions are preserved. Originally, England and Richardson (1977) showed that blueschist facies mineral assemblages are more likely to be preserved in mountain belts and in metamorphic belts where uplift is relatively fast. If uplift rates are not rapid enough, thermal relaxation will result in over-printing of the early-formed blueschist assemblages with overprinting greenschist- to- amphibolite facies assemblages (Fig. 7.1); the rocks need to be exhumed before they have time to rise in temperature too far. Rapid uplift as a means of preserving blueschist facies assemblages was investigated further by Draper and Bone (1981). This study also showed that low rates of heat production and heat flow were effective in the preservation of blueschist facies assemblages.

An alternative mechanism for low temperature-high pressure metamorphism is the under-thrusting of the crust, in which metamorphism is occurring, by cold, dense crust in which the rate of heat production is low. The study of Rubie (1983) is a good example, in which blueschist facies assemblages in the Western Alps are preserved by the subduction of cold ocean lithosphere under continental crust. Other examples of this kind of model are Goffe and Velde (1984), Davy and Gillet (1987) and Gillet and Goffe (1988), which also show that the thermal evolution of thrust slices over short time scales depends critically on the number of thrusts and on the duration of thrusting (see also Karabinos and Ketchum 1988, in press).

The preservation of high-pressure low-temperature assemblages in the South West Highlands as a result of rapid uplift rates can be ruled out, however, because the petrological, and geochronological data show that cooling rates were slow (section 3.4, chapter 6), at ca. 3 °C per Ma, in comparison with up to 20 °C per Ma in the Alps (eg Hawkesworth et al. 1976) and between 5 and 20 °C per Ma in th Perthshire and Angus Dalradian (Dempster 1985). Preservation of these
regional metamorphic assemblages by the subduction of cold ocean lithosphere is also unlikely, because the absence of Dalradian detritus in the Highland Border Series ophiolites suggests that the ocean crust now present in these rocks was far away from the Dalradian at the time of D₁ to D₃ deformation (Curry et al. 1984, Bluck 1985: cf. Dewey and Shackleton 1984). Furthermore, there is little or no geophysical evidence for the presence of ocean lithosphere beneath the present Dalradian crust.

The other mechanism for the production and preservation of high pressure-low temperature regional metamorphic assemblages is by low rates of crustal heat production and heat flow from the mantle. The models of England and Richardson (1977) and Draper and Bone (1981) both suggested that blueschist facies P-T conditions are more likely to be produced if heat production rates are low, and the types of models exemplified by Rubie (1983) essentially examine the behaviour of thickened crust whose mean heat production rate is lowered by the subduction of cold crust of low heat production rates beneath the crust undergoing metamorphism. In the most comprehensive study of the thermal evolution of thickened continental crust made so far, England and Thompson (1984) show that P-T conditions similar to those found in the primary assemblages of the South West Highlands are produced in crust with low heat production and moderate to high conductivity (Fig. 7.2), the heat production rates being 4 HGU (1.667 μW m⁻³) in the first 20 km depth of the unthickened crust, instead of the "normal" heat production rates of 4.75 HGU, or 2μW m⁻³, and conductivities of 6 to 7 mCal cm⁻¹ K⁻¹, or 2.25 to 3.0 Wm⁻¹ K⁻¹.

It has already been shown, in chapter 2, that the major difference in the large scale deep crustal structures and compositions between the South West Highlands and the Central Highlands is due to the absence of metasedimentary rocks between the Dalradian and the base of the crust in the South West Highlands, where the Dalradian is separated from the lower crust by a large wedge of high grade gneiss, tapering and thinning to the south-east, based on interpretation of the WINCH profile (Hall 1985, section 2.3). This wedge is probably exposed in Western Islay (see also Westbrooke and Borradaile 1978) and is likely to have been cool when emplaced, due to the absence of significant metamorphism in the sediments immediately prior to Caledonian deformation (Fitches and Maltman 1984, see also section 7.2.3).

The Northern Kintyre area, with its more complex structural and
Fig. 7.2 Some of the model P-T-t paths of England and Thompson (1984) for homogeneously thickened crust. Lower peak temperatures result from lower rates of radiogenic heat production. Note that the path marked passes through the P-T conditions of the primary metamorphism in the South West Highlands (from England and Thompson 1984).

Fig. 7.3 Heat transfer by conduction in a homogeneous medium: the heat flux through a point in the medium is proportional to the temperature gradient at that point (from Turcotte and Schubert 1981).
metamorphic history, also has the crust with the lowest proportion of rock with low heat production rates. This area exposes the deepest structural levels and cooled through given temperatures up to 30 Ma later than in Knapdale and Tayvallich. As a result, the thermal evolution of Northern Kintyre should show strong contrasts with that of Knapdale and Tayvallich. These contrasts will therefore also be investigated by thermal modelling.

It needs to be stressed here that the models produced in this chapter are not intended to be a complete and rigorous description of the regional metamorphic processes which occurred in the South West Highlands. They are intended to indicate the major controls on P-T-t histories only, by attempting to mimic the P-T-t histories derived and presented in previous chapters, and specifically, to find out how long the rocks need to be held at depth before significant heating can occur, given the constraints imposed by the measured thermal properties (table 7.1, Richardson and Powell 1976), and whether the necessary resulting cooling rates are consistent with the slow cooling rates observed. Because the P-T-t histories are well constrained from petrological and geochronological data, the results produced by the models, though they probably will not be unique, will give a good indication of what the controlling influences on the contrasting regional metamorphic histories are. Obviously, it is easy to select parameter values to produce the results desired, so the sensitivity of the results to the more variable input parameters will be assessed.

7.2 Heat Flow Modelling; Starting, Running, and Boundary Conditions:

Prior to the presentation of the results from the thermal modelling, the assumptions, input parameters, and boundary conditions are discussed in this section, which will include a review of the mathematical analysis used in the models, and a more formal derivation of the structure and thermal properties of the crust, based on the information and constraints available from the geophysical evidence, discussed in chapter 2.
7.2.1 Heat Transfer Mechanisms in the Continental Crust:

Heat transfer in the crust can take place by conduction or by advection. Though many theoretical studies of advective heat transfer by fluid flow show that this can be a significant means of heat transfer (Chamberlain and Rumble 1988, in press, Brady 1988, in press, Bickle and McKenzie 1987), these studies show that such heat transfer tends to occur only over short time-scales, and will be localised. Any model which includes advective heat transfer by fluid flow is therefore likely to be over-specified with respect to the constraints available on P-T-t histories in the South West Highlands.

Conduction is the mechanism of heat transfer modelled by England and Richardson (1977) and by most subsequent modelling of regional metamorphism (eg England and Thompson 1984, Dempster 1985). Heat is transferred as a result of the perturbation of an equilibrium temperature gradient in the crust by a large scale tectonic event; the changing temperature distributions in the crust over time are due to the re-equilibration of the disturbed thermal structure resulting from the rapid tectonic event. The thermal structure of uplifting, thickened crust changes constantly due to the long time-scales of conductive heat transfer over 10 to 100 Km length-scales. If crust-sized masses of rock are moved at mm per year velocities, heat advection will occur over these length-scales. It is for this reason that the temperature-depth profile in crust undergoing regional metamorphism and deformation is never constant, as was assumed prior to England and Richardson (1977, see also chapter 1).

In a homogeneous, stationary medium with no internal heat production, the heat flux, q, as a result of heat transfer by conduction is given by

\[ q = - K \frac{\delta T}{\delta X} \]  

(1)

where \( K \) is a constant, the conductivity of the medium, and the term in brackets is the temperature gradient across the medium. Thus, the rate of heating or cooling at a point is proportional to the temperature gradient at that point (Fig. 7.3). Equation (1) is the basic law of conductive heat transfer. The time-scales, \( t \), and the length-scales, \( l \), of conduction are related by

\[ l^2 \approx Kt \]  

(2)
These two expressions taken together show how a short length-scale thermal anomaly has a relatively short life-time, because such a thermal anomaly will decay rapidly due jointly to its short length-scale, and the steep temperature gradients that will be associated with it. As a result, crustal scale thermal structures produced by regional deformation and orogeny will have relatively long life-times, decaying and equilibrating over long time-scales. Thus, any thermal model, and any means of heat transfer invoked for crustal-scale metamorphic processes must be capable of sustaining the temperatures and heat flow concerned for long periods of time. In the case of the South West Highlands, timescales of crustal heating and cooling are of the order of 100 Ma, based on the cooling age data in chapter 6.

The advection of heat by the movement of rock, rather than fluid or magma, has been recognised as being a significant means of heat transfer in a number of studies (eg Chamberlain 1986, Fisher 1980), and has been modelled by Sleep (1978). For the inversion of isotherms to occur (see also chapter 3), heat needs to be advected (eg LeFort 1975). All the models for heat advection imply that it is necessarily a transient process with time-scales of less than 10 Ma (eg Shi and Wang 1987, Peacock 1987). The heating and cooling patterns that would result from such mechanisms are therefore unlikely to be resolvable if they had been in operation in the South West Highlands. In addition, the calculations presented by Crowley (1987) show that rapid cooling rates are necessary for the preservation of the thermal structure produced by heat advection as metamorphic isograds.

The models presented in this chapter assume that the dominant means of heat transfer over crustal length-scales and 10 to 100 Ma time-scales is by conduction. This is because the data available to constrain the models concern changes in P-T conditions with time over these length-scales and time-scales only. Models which examine shorter length- and time-scale heat transfer processes will be over-specified with respect to the information available. Specifically, heat transfer is assumed to occur in one dimension only, that is vertically. The modelling of heat flow by conduction in one dimension is justified only if it is clear that horizontal heat transfer is likely to be insignificant in comparison to vertical heat flow; this assumption will be assessed further below.

The models of England and Richardson (1977) and England and Thompson (1984) assume one-dimensional heat flow. In the case of the South West Highlands, at the time of the primary metamorphism, and assuming that this
occurs at about the same time throughout the region, the vertical temperature gradient would be about 15°C per Km, while the across-strike horizontal temperature gradient between South Knapdale and Tayvallich would be less than 5°C per Km, in that there is about 100°C difference in metamorphic temperature over 20 Km distance across-strike (chapter 5). The attitude of the bedding has been steepened by D_4/B_2 deformation, which probably occurred up to 100 Ma after the primary metamorphism, so the highest grade rocks would have been horizontally further away from the lowest grade rocks than they are now. Thus, the rate of horizontal heat transfer is unlikely to have been more than 20% of the rate of vertical heat transfer, assuming that the vertical and horizontal conductivities were similar.

The effect of horizontal heat transfer would be to increase the cooling rates in the higher grade rocks and reduce the cooling rates in the lower grade rocks (cf. Ridley 1988, in press). Clearly, if there was some conductive anisotropy in the rocks, the flat-lying attitude of the bedding and schistosity after D_1-D_2 deformation would result in the higher conductivity direction being near to the horizontal, thus increasing lateral heat transfer rates. The models to be presented assume one-dimensional heat flow and therefore must be interpreted with some caution (see also 7.4.2).

7.2.2 Heat Conduction Modelling; Methods and Mathematics:

The conduction of heat, in one dimension, through a homogeneous stationary medium with no internal heat production, is governed by equation (1) above. The problem is rendered mathematically more complex for the situation of interest in this chapter because rocks will be inhomogeneous, and thickened continental crust will be moving due to erosion. In addition, rocks have internal heat production, by radioactivity and by deformational and shear heating (eg Graham and England 1976, Brewer 1981). Deformational and shear heating will be transient in relation to conductive heat transfer, so is therefore unlikely to be resolved on the scales of interest in this study. The conduction of heat through a moving medium with internal heat production is given by

\[ pC_p(\delta T/\delta t) = K(\delta^2 T/\delta X^2) + (\delta K/\delta X \cdot \delta T/\delta X) + U_x pC_p(\delta T/\delta X) + Q_{x,T,t} \]
where $P$ is the density of the medium, $C_p$ is the heat capacity of the medium at constant pressure, $T$ is temperature, $t$ is time, $x$ is length, $U_x$ is velocity in the $x$ direction and $Q$ is the rate of internal heat production. In the case modelled in this chapter, $U$ is the uplift rate, and $x$ is the depth. This equation is solved numerically using a Crank-Nicholson finite difference method (see also Ridley 1982, pp 246-248). The boundary conditions are a fixed value for heat flux through the lower boundary, and a fixed temperature of $0^\circ C$ at the upper boundary. The initial conditions of the models are derived in 7.2.4 below. Thermal models of regional metamorphism indicate that large-scale disequilibrium in the crustal temperature distribution is a necessary initial condition, such disequilibrium being produced by rapid deformation. The consistency of this assumption is assessed next, along with means by which temperature disequilibrium might have been produced in the South West Highlands.

7.2.3 Causes of the Regional Metamorphism:

Thermal models of regional metamorphism require that thermal dis-equilibrium over crustal length-scales be present as one of the starting conditions. The most convenient way of producing such a disequilibrium feature is by rapid thickening of the crust, a process that is seen to be occurring in young mountain belts. The models of England and Richardson (1977) and England and Thompson (1984) showed how Barrovian facies series regional metamorphism is triggered by crustal thickening and subsequent erosion, the crustal radiogenic heat production rates usually being sufficient to allow attainment of the necessary temperature-depth conditions.

The primary metamorphism in the South West Highlands was clearly a very major tectonothermal event, with pervasive deformation, reversal of stratigraphy, regional isoclinal folding and the emplacement of nappes. The episode has probably affected the entire Scottish Dalradian, not just the South West Highlands, but so far little information or constraint is available on what the cause of this event was. The observation that the primary metamorphism took place
during the D_1-D_2 deformation made in section 3.4 shows that the Tay Nappe emplacement took place when the crust had already been thickened, hence that the Tay Nappe emplacement was **not** the primary thickening event which brought about Dalradian regional metamorphism. Possible models for the cause of Dalradian regional metamorphism are now considered.

### 7.2.3.1 Models for Dalradian Regional Metamorphism:

A bold attempt to explain the Tay Nappe was that of Dewey and Shackleton (1984) who suggested that a huge ophiolite nappe was emplaced from the south-east over the Dalradian sedimentary pile during D_1-D_2 deformation, the remnants of this nappe being preserved in the Highland Border Series ophiolites, the Clew Bay ophiolite, Newfoundland, the Ballantrae ophiolite, Southern Scotland, and the Solund ophiolite in Shetland. This model requires that the Highland Border Series ophiolites are older than any of the deformational phases in the Dalradian, since they contain little or no Dalradian detritus in their sedimentary components, and were therefore far away from the Dalradian sedimentary pile, prior to their tectonic emplacement. The fauna found in the Highland Border Series (Curry et al. 1984) indicate that the sediments are in fact of similar ages to the Dalradian deformation and metamorphism, so these ophiolite fragments could not have been emplaced onto the Dalradian at the time of D_1-D_2 deformation.

The timing on which this model was based was derived from Dewey and Pankhurst (1970), and has therefore been largely superseded by more recent information on the timing of metamorphism, heating, and cooling in the Dalradian (Dempster 1985, Pidgeon and Aftalion 1978, this thesis, chapter 6) all of which shows that Dalradian heating and cooling occurred over a longer period of time than that inferred by Dewey and Shackleton (1984), who suggested a time for D_1-D_2 deformation of ca. 500 Ma ago, and for D_3 deformation of ca. 475 Ma ago. Both these timings are about 30 Ma too young, based on the timing in the references just cited.

Finally, the model requires that the initial thickening of the Dalradian occurs at about the same time as the D_1-D_2 deformation, which is obviously at variance with the requirement for the Dalradian to be at temperatures of up to 525°C, at this time. The cause of Dalradian metamorphism must therefore be looked for elsewhere.
7.2.3.2 Suspect Terrains in the Scottish Caledonides:

Bentley *et al.* (1988), in presenting new information on the structures on Islay and Colonsay (see also Fitches and Maltman 1984, this thesis, section 2.5), suggested that Colonsay and West Islay are exposures of a tectonically-bounded block whose deformational and sedimentological histories are distinct from those of the rest of the Scottish Caledonides, this block therefore forming a suspect terrain.

Bentley *et al.* discuss the correlation of the Bowmore and Colonsay groups with sedimentary sequences on the mainland, with unconstrained correlations with the Moine (Roberts 1974), Dalradian (Fitches and Maltman 1984), and Torridonian (Cunningham-Craig *et al.* 1905) having been made. In addition, the high grade basement gneiss on West Islay is geochemically distinct from the Lewisian gneiss in the north-west of Scotland, according to observations cited by Bentley *et al.* (1988). These observations are supported by new isotopic data (Marcantonio *et al.* 1988), showing that the West Islay basement is entirely Proterozoic in age, at about 1700 to 1800 Ma old, in contrast to the late Archean age of the Lewisian (eg Moorbath *et al.* 1969).

The major difference, however, between the geological history of the West Islay-Colonsay block and the Dalradian on the mainland is the presence of a deformational phase which pre-dates the Dalradian D₁-D₂ deformation. Bentley *et al.* suggest that this event occurred before 600 Ma ago, based on Ar-Ar ages on amphiboles separated from igneous intrusives in which are found xenolithic fragments of country rocks with pre D₁-D₂ fabrics and structures. No details of the age data are given in Bentley *et al.* (1988), so assessment of the geochronological data on which this timing is based is difficult. In principle, an Ar-Ar age on amphiboles should give a minimum emplacement age for the intrusive rocks concerned, because they underwent Dalradian biotite grade metamorphism (sections 2.5, 3.1). However, without these age data, it would be tempting to suggest that the pre-D₁-D₂ deformation on Colonsay and West Islay equated to the thickening episode that brought about Dalradian metamorphism. The pre-600 Ma timing for this deformation suggested by Bentley's unpublished data is obviously inconsistent with the time constraint on Dalradian deposition of Halliday *et al.* (1988, in press; see also section 2.4), so the validity or otherwise of the age data quoted by Bentley *et al.* (1988) assumes particular importance.
Bentley et al. (1988) suggested that the emplacement of the suspect terrain against, or beneath, the Dalradian sedimentary pile would have occurred between 600 Ma, based on their Ar-Ar age data, and 540 Ma, based on the Rb-Sr whole-rock errorchron of Leggo et al. which is suggested as timing the primary metamorphism in the Dalradian in East Islay. Though the errorchron just mentioned would normally be extremely ambiguous, the resulting age happens to be consistent with the timing for Dalradian primary metamorphism suggested, based on the geochronological data presented in chapter 6, as occurring before 525 Ma. Thus, the suggested timing of emplacement of the West Islay-Colonsay terrain brackets neatly the time available for burial and heating of the Dalradian sedimentary sequence, which necessarily needs to have happened before 525 Ma, and after 600 Ma ago, based on Halliday et al. (1988, in press).

The WINCH line, as has been described in section 2.3 and by Hall (1985) shows that the rock now exposed on West Islay and Colonsay, the basement gneiss, and the Bowmore and Colonsay Group sandstones, are emplaced beneath the Dalradian along south-east dipping reflective horizons, inferred to be thrust planes. A similar relationship was inferred by Westbrook and Borradaile (1978) from aeromagnetic mapping. As a result, the basement gneiss and overlying sandstones form a wedge thinning to the south-east beneath the Dalradian of Knapdale and Northern Kintyre. The contact between this gneiss wedge and the Dalradian is the West Islay Shear Belt, known from structural mapping (Fitches and Maltman 1984, see also section 2.4) to have been active during D1-D2 deformation. Thus, much of the emplacement of this gneiss wedge would have occurred during the primary deformation, which made up the main phase of nappe emplacement in the Scottish Caledonides. Thus, whatever the status of the West Islay-Colonsay terrain, its contact with the Dalradian is continuous at depth beneath most of the South West Highlands.

It is at present unclear, how much of the emplacement of the basement gneiss wedge occurred prior to, or during, D1-D2 deformation, but if a significant amount of the emplacement occurred before the primary deformation, this might have been associated with the crustal thickening episode which ultimately resulted in the Dalradian regional metamorphism. The more likely alternative, that most of the emplacement of the gneiss wedge occurred during the primary deformation implies that this emplacement probably caused the nucleation and propagation of the Tay Nappe, hence the resulting primary metamorphism. The resultant
disturbance to the thermal structure of the crust at the time of a possible syn-D₁-D₂ emplacement of this gneiss wedge would have been profound, and might have triggered cooling.

The speculations in the above paragraph are unconstrained at present, but the alternatives have been modelled and the results will be presented in this chapter. Essentially, if the Ar-Ar age data quoted by Bentley et al. (1988) are accurate, the pre D₁-D₂ crustal thickening episode inferred to have caused Dalradian metamorphism has left no apparent sign of its occurrence in the rocks affected, or in any other region that is associated with the tectonothermal history of the Dalradian. The Ar-Ar age data, would normally be considered accurate, since the ages are from amphiboles which are generally thought to have a relatively high closure temperature (section 6.1). However, ages on the pre-D₁-D₂ fabrics are lacking, and would provide very important, and perhaps less ambiguous, constraints on the timing of this deformation.

The thermal models to be presented in this chapter should therefore help to constrain the possibilities and speculations in this subsection. Emplacement of the terrain as a gneiss wedge at the time of D₁-D₂ deformation, when the overthrust Dalradian crust was relatively warm, would have differing thermal consequences to emplacement of the same gneiss wedge at the time of initial thickening, when the overlying Dalradian crust was still relatively cool. These contrasts will be apparent in the heating times necessary between initial thickening, and attainment of syn-D₁-D₂ P-T conditions. This is because the two alternative scenarios either involve the gneiss wedge being present throughout the tectono-metamorphic history of the Dalradian (emplacement during initial thickening), or for part of the tectono-metamorphic history of the Dalradian (emplacement during D₁-D₂ deformation). Thus, the timing of the initial crustal thickening event necessary to bring about Dalradian regional metamorphism will be inferred solely from the models, and will therefore provide an effective test for the two alternatives.

The other unknown factor is the temperature of the gneiss wedge when it was emplaced. The presence of biotite in the Bowmore and Colonsay Groups shows that these rocks reached temperatures of at least 350°C at some stage in their metamorphic history. However, if the Bentley et al. (1988) Ar-Ar data from amphiboles are accepted, these imply that the Bowmore and Colonsay Groups were previously at temperatures high enough for deformational fabrics to be formed at least 70 Ma prior to the primary deformation, and hence that the gneiss wedge

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with over-riding sediments was probably cool on emplacement beneath the Dalradian crust. As with the differing times of emplacement, differing temperatures in the under-thrust wedge will have major consequences for the subsequent thermal evolution of the thickened crust. The models to be presented will therefore provide a test for the temperatures of the gneiss wedge on emplacement, in turn giving a possible indication of how long before primary deformation the pre-\(D_1\) \(D_2\) deformation occurred.

There will therefore be three classes of model made in this chapter:

The class I models assume that the gneiss wedge was emplaced during the initial thickening episode, hence implying that this thickening was caused by the gneiss wedge emplacement; these models will also assume that the wedge was warm at the time of emplacement, with its upper surface being at the same temperature as the base of the over-thrust Dalradian, and temperature-depth gradients being equal to those in the Dalradian crust (see also 7.2.4.2). The class II models will assume that the gneiss wedge was emplaced at the time of initial thickening, but was cool at the time of emplacement, with its upper surface being held at a temperature of \(0^\circ C\) and with a temperature-depth gradient equal to that in the over-thrust Dalradian crust. The class III models will assume a cool gneiss wedge under-thrust at the time of \(D_1\) - \(D_2\) deformation. The temperatures in the wedge will be varied in different class III models.

The extent to which isotherms might be deflected during the emplacement of the Tay Nappe was speculated upon in section 3.6. Essentially, significant advection, with a possible subsequent effect on regional cooling rates would occur if strain rates during nappe emplacement were high enough. However, subsequent relaxation of isotherms would occur over short time-scales, preventing formation of inverted isograd sequences unless post metamorphic cooling rates were rapid. All the petrological and geochronological evidence in the previous chapters shows that post-primary metamorphic cooling rates were slow, thus making it unlikely that the emplacement of the Tay Nappe would affect the P-T-t history of the region over longer than 10 Ma time-scales. This is because the temperature contrasts between the over-thrust and under-thrust rocks would be too small to cause a major cooling and heating effect.

The class III models, however, are based on the premise that the under-thrust gneiss wedge was cool enough to have a significant effect on subsequent crustal thermal structures. Some of the class II models are attempts to account for possible rapid cooling caused by nappe
emplacement; more advanced treatment is beyond the scope of the thermal model used in this chapter.

7.2.4 Initial Conditions of the Thermal Models:

The initial conditions of the thermal models are those parameters whose values are set in the models at the start of the processes that are being examined. These parameters may then either vary or remain constant during the modelling. The parameters of interest in the modelling of regional metamorphism are the initial temperature gradient, the conductivities, heat production rates, the thicknesses and the densities of the rocks in the crust to be modelled. Thus, the values of these parameters for the South West Highlands will be estimated from geophysical information on the deep crust (section 2.3), and the published measurements of thermal properties of Dalradian lithologies (Richardson and Powell 1976). The range in pressures of metamorphism of 9 to 12 Kbar imply an initial depth of burial of at least 32 to 40 Km. Uncertainties will arise, however, because much rock has been eroded whose composition and thermal properties are unknown. Essentially, the thermal properties of the lower half of the original thickened crustal pile at the time of regional metamorphism is constrained. However, the models will be less sensitive to the properties of the top of the crust being modelled than those of the base of the crust for two reasons; the top of the crust will be removed at an early stage of the uplift history by erosion, and the heat build-up from high heat producing rock nearer the surface will be reduced due the proximity to the cool surface.

7.2.4.1 Initial Temperature Distributions:

The initial temperature profile in the crust prior to regional metamorphism is unconstrained. The equilibrium temperature-depth profile, or geotherm, of continental crust is the balance between rates of heat accumulation, by heat flux though the lower boundary and radiogenic heat production, and rates of heat loss by conduction through the upper boundary. Thus, by measuring heat fluxes and making reasoned assumptions about the distribution of radioactive elements with depth, the geotherm present in the crust at the time of measurement can be calculated. Most published temperature-depth and depth-heat production rate distributions are derived from continental shields. This is because these areas are well constrained thermally, are homogeneous, and have had time to reach thermal
equilibrium due to their great age. However, the Dalradian is heterogeneous on all scales, due to the variety in the depositional history and composition of the crust in the region (chapter 2). As a result, temperature-depth and heat production rate-depth distributions from shield areas are not appropriate for the Dalradian. In addition, one of the hypotheses being tested by the models is that variations in the crustal composition influenced the metamorphic history in the South West Highlands; contrasting depth-heat production distributions must be included in the models.

While it would be relatively easy to calculate an equilibrium temperature-depth profile for the Dalradian sedimentary sequence prior to burial, using estimated heat production rates for the various lithologies present, the Dalradian sedimentary basin had tholeitic rift volcanics associated with it (Graham 1976), with primary metamorphic assemblages growing within 60 Ma of the cessation of active volcanism. The presence of tholeitic volcanics implies a localised stretching B factor of at least 5 (R. Scrutton, D. Latin, pers. comm.s). Thus, there would have been an enhanced temperature-depth profile during sedimentation. This temperature-depth gradient would decay exponentially with a time constant of about 60 Ma (eg McKenzie 1977), so the value of this gradient at the time of initiation of Caledonian orogenic processes depends on how soon after the cessation of active volcanism these processes started.

The models of England and Richardson (1977) and England and Thompson (1984) between them examined the thermal evolution of crust thickened by instantaneous thrusting, and by homogeneous thickening of the whole crust, and of the whole lithosphere (including the crust). The models were insensitive to the assumed mode of initial thickening because the disequilibrium temperature-depth profile decays into a smooth geotherm with a depressed temperature-depth gradient within 2 Ma of the rapid initial thickening. The homogeneous thickening models tended to produce slightly lower peak temperatures at given depths because these models concentrated the higher heat producing crust near the top of the thickened pile, while the thrusting models had higher rates of heat production at greater depths, hence further away from the upper boundary. However, the differences between peak temperatures resulting from the various thickening scenarios were relatively small compared with random and systematic errors associated with geothermometry, so that the initial mode of thickening assumed will not introduce large errors into the calculations.
Using the conductivities and heat production rates of Richardson and Powell (1976) for crust comprising the lithologies present in the South West Highlands, and allowed to reach thermal equilibrium, results in geotherms with gradients of about 15 to 20°C per Km. Doubling the thickness of the crust homogeneously will therefore give a depressed geotherm of between 7.5 and 10 °C per Km. Gradients of 7.5 and 10 °C per Ma will therefore be used for the initial geotherms in the models, as well as a more enhanced geothermal gradient of 15 °C per Km in the thickened crust to test the sensitivities of the results to possible enhanced heat flux through the lower boundary due to basin activity prior to burial of the sedimentary pile. The heat flux through the lower boundary, during the running of the models, will also be varied, again to test the sensitivity of the models to variations due to basin activity.

7.2.4.2 Thermal Properties of the Crust:

The thermal properties of the crust are the conductivities, heat capacities and rates of heat production. While the heat capacities of the rocks in the crustal pile are calculated after England (1979), the heat production rates and conductivities are derived from Richardson and Powell (1976), and the crustal structure modelled is derived from the interpretation of Hall (1985) of the WINCH seismic reflection data.

(a) Specific Heat Capacities: The heat capacities of the crust being modelled are assumed to obey the empirical function with temperature derived by England (1978). This function is a fit to measurements made in a number of studies of various lithologies and is given by:

\[ \text{cp} = 0.18 (1 + 6.14 \times 10^{-4} T - 1.928 \times 10^4 / T^2) \]

where T is the temperature in Kelvins and heat capacities are measured in cal gm\(^{-1}\) K\(^{-1}\).

(b) Heat Production Rates: Fig. 7.4 (a) shows simplified "layer-cake" sections through the present-day crust at Tayvallich, South Knapdale and Northern Kintyre. The heat production rates, densities, and conductivities of mafic rock, Erins Quartzite, Crinan Grit, Ardrishaig Phyllite and Beinn Bheula Schist are as given on table 7.1. Heat production rates of the basement gneiss wedge, thrust beneath the Dalradian, is taken to be zero, based on numerous observations of the
Fig. 7.4 (a) Simplified “layer cake” models through the present-day crust in the South West Highlands, with the thermal properties of the lithologies present: models are for (i) the biotite zone of Tayvallich, (ii) the garnet zone of South Knapdale, and (iii) Northern Kintyre.

(b) Interpretation of the crustal structure in the South West Highlands derived from the WINCH profile (from Hall 1985).

Fig. 7.5 Model of Borradaile and Hermes for variation in heat flow through the South West Highlands as a result of conductive anisotropy and the regional orientation of schistosity (from Borradaile and Hermes 1979).
Table 7.1 Heat production rate measurements of Richardson and Powell (1976) for Dalradian lithologies similar to those present in the greatest abundances in the South West Highlands: the average Dalradian value is that calculated by Richardson and Powell from their measurements: it is much higher than the values for the lithologies quoted in this table.

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Heat production rate (H.G.U.) at ca. 500 Ma ago</th>
</tr>
</thead>
<tbody>
<tr>
<td>hornblende schist</td>
<td>0.78</td>
</tr>
<tr>
<td>gt-semipelite</td>
<td>2.55</td>
</tr>
<tr>
<td>semipelite</td>
<td>1.99</td>
</tr>
<tr>
<td>gt-pelite</td>
<td>2.50</td>
</tr>
<tr>
<td>gt-semipelite</td>
<td>1.58</td>
</tr>
<tr>
<td>psammite</td>
<td>1.68</td>
</tr>
<tr>
<td>bi-phyllite</td>
<td>1.72</td>
</tr>
<tr>
<td>average Dalradian</td>
<td>4.0±2.1</td>
</tr>
<tr>
<td>average Moine</td>
<td>4.1±1.5</td>
</tr>
</tbody>
</table>
Depletion of granulite facies terrains in heat-producing elements (e.g. Tarney and Windley 1977). This assumption follows that of England and Thompson (1984, p. 896, equation (1)). The thicknesses of the crustal layers in each of the three areas to be examined was measured from Fig. 6 of Hall (1985) (Fig. 7.4(b)). The high proportion of rock in the crust in the north-west (Knapdale and Tayvallich) with low to negligible heat production rates is clearly illustrated in this figure.

(c) Conductivities: The main previous model of regional metamorphism in the South West Highlands is the attempt of Borradaile and Hermes (1980) to explain the regional isograd distribution. This model suggested that the highest grades of metamorphism were developed in areas where the heat flow was highest due to the attitude of regional schistosity (Fig. 7.5). This interpretation was based on anisotropic conductivity in schistose lithologies, but was also based on a distribution of isograds now known to be incorrect (chapter 3), in that the garnet zone was said to be restricted to South Knapdale, as drawn on the map of Fettes et al. (1979). In addition, the model assumed that the heat source for regional metamorphism is found below the rocks being metamorphosed, rather than from radiogenic heat production within the rocks. The model also suggested that the primary metamorphism post-dated the formation of the Knapdale Steep Belt, now believed to have occurred during D₄/B₂b deformation (chapter 2, Roberts 1974). All available thermal models of regional metamorphism show that increasing conductivity results in lower peak temperatures, because heat is lost more easily from the rocks on thickening.

However, the model of Borradaile and Hermes (1980) does draw attention to the importance of the attitude of the bedding and regional schistosity during primary metamorphism. It has been suggested in chapter 3 that the Tay Nappe was inclined during the primary metamorphism; support for this suggestion is found in the P-T conditions of primary metamorphism derived in chapter 5. From these P-T conditions, the Tarbert area was probably at least 3 km deeper in the crust than the Tayvallich area, with Northern Kintyre, in turn, buried at least 3 Km deeper still. The relative depths of burial during the primary metamorphism imply a relatively shallow, but uniform, attitude of the bedding and schistosity during the primary metamorphism. Despite the presence of pervasive D₃ deformation in the early secondary metamorphic assemblages, no D₃ regional folds have been recognised in the South West Highlands so far. It is therefore unlikely that steepening of the regional schistosity, and formation of the Knapdale
Steep Belt as a result, has occurred before the $D_4/B_2$ deformation. Thus, it is probable that the attitude of the regional schistosity was preserved throughout the primary and the earlier stages of the secondary metamorphism, and that this schistosity dipped at a shallow angle towards what is now the north-west. Thus, the vertical conductivity of given lithologies is unlikely to vary across the region. However, as mentioned earlier, the horizontal conductivity in the Dalradian may well be higher than the vertical conductivity.

### 7.2.4.3 Uplift Rates:

The uplift rates are calculated on the basis of the pressures of metamorphism derived in chapter 5 for the primary and secondary episodes, along with the geochronological data in chapter 6. The primary metamorphism occurred at pressures about 3 Kbar higher than those of the earlier stages of the secondary metamorphism, and up to 30 Ma earlier. This change in pressure translates to an average uplift rate of about $0.33 \, \text{km Ma}^{-1}$ for the south-east of the area. The biotite zone was metamorphosed at pressures about 1 Kbar lower than the garnet zone, but cooled through 350 to 400°C (the closure temperature for Ar in phengite) roughly simultaneously with the garnet zone. The garnet zone therefore probably uplifted more quickly between 535 and 475 Ma than the biotite zone.

In the biotite and lower garnet zones, post-primary metamorphic P-T conditions are not well constrained due to the absence of secondary assemblages. However, the probable absence of steepening (Steep Belt formation) prior to $D_4/B_2$ deformation suggests that uplift rates were similar to, or slower than, those to the south-east. The later cooling of the Northern Kintyre area through given temperatures implies that this area may have uplifted more slowly than Knapdale at some stage in its uplift history. After 500 Ma, uplift rates were similar to, or lower than, those prior to 500 Ma, since the pressures of the later stages (k-feldspar + chlorite growth) of secondary metamorphism were again about 2 to 3 Kbar lower, the latest stages in secondary metamorphism occurring at 440 to 450 Ma. Uplift rates therefore varied between 0.2 and 0.4 Km per Ma throughout the area’s P-T-t history.

Thus, realising the potential for subjectivity in modelling (choosing input parameters to suit the desired conclusions), modelling is to be carried out using a range of parameters, especially where these are poorly constrained, to test the sensitivity of the results to these uncertainties. The results of the models are
presented in the next section.

7.3 Heat Flow Modelling; Results and Interpretations:

The input and running conditions to be used in the thermal models were discussed in the previous section. The results of these models are now to be presented. The section is in three parts, one part for each of the Tayvallich, South Knapdale and Northern Kintyre areas.

7.3.1 Thermal Models for Tayvallich:

The P-T conditions of metamorphism in Tayvallich were in the range of 420 to 450°C, and 10 Kbar. The thermal models for the biotite zone therefore need to produce P-T-t paths that pass through these points in P-T space, at some, as yet undetermined, time after crustal thickening, assumed to have occurred rapidly, and which do not continue to rise in temperature far beyond the temperatures preserved in the assemblages. In addition, the rocks are constrained by cooling age data to have cooled through ca. 350 to 400°C about 70 Ma after attainment of the biotite zone P-T conditions.

The problem intended to be resolved by the thermal modelling, that of the preservation of P-T conditions normally associated with the blueschist facies in an area that underwent slow cooling is particularly acute in the biotite zone. As a result, the models for the biotite zone will hold the key to the resolution of this problem. Several models have been made, and will be presented, with varying starting and running conditions. The heat production rate and conductivity distributions, and crustal thicknesses are similar in all the models produced.

7.3.1.1 Class I models:

Two model P-T-t paths resulting from class I models are presented in Figs 7.6 and 7.7. The first model (7.6) assumes an initial geotherm of 7.5°C per Km, while the second (7.7) assumes a 10 deg C per Km initial geotherm. Of these two models, the first results in P-T-t paths passing through the correct P-T conditions of the primary metamorphism (\((P-T)_{S_{\text{max}}})\), but continuing to rise in temperature subsequently. The second model, in contrast, results in peak temperatures higher
Fig. 7.6 Class I model with initial temperature distribution on a temperature gradient of 7.5° C/km: heat production rates as Fig. 7.4(a):
Fig. 7.7 As Fig. 7.6 but with initial temperature gradients of 10° C/km: the box shows the array of primary metamorphic P-T conditions in the biotite zone assemblages.
than 425°C at all times in the P-T-t trajectory while uplift rates are significant, and while the pressure is greater than 6 Kbar. Thus, while the first of these models reproduces the P-T conditions of metamorphism, the second does not without exceeding 450°C subsequently. Though this class of models can reproduce the correct (P-T)Smax conditions, they can only do this if the heat flux through the lower boundary is not enhanced. These models do not therefore allow for the possibility of enhanced geothermal gradients and heat fluxes resulting from relaxing geotherms from basin activity at the time of crustal thickening.

7.3.1.2 Class II models:

Modelled P-T-t paths for a variety of starting and running conditions are presented in Fig.s 7.8 to 7.13. Fig. 7.8 is for crust with initial geothermal gradients of 10°C per Km. The P-T-t trajectory starting at a depth of 37.5 Km passes through 9 to 10 Kbar and 425°C about 35 Ma after thickening. This trajectory then passes through 350°C 100 Ma after the thickening, or about 470 Ma ago. This P-T-t path therefore reproduces the P-T-t history of the biotite zone at Tayvallich accurately. However, as with the previous models, the peak temperatures are reached after passage through (P-T)Smax.

Fig.s 7.9 and 7.10 are for models investigating the effects of changing the lower boundary heat flux. Increasing this to 1.0 HFU from 0.8 HFU results in peak temperatures in excess of 500°C for the rock whose initial burial depth was 37.5 Km (Fig. 7.9). In contrast, lowering the heat flux to 0.6 HFU (Fig. 7.10) results in peak temperatures of less than 400°C for the rocks buried at 37.5 Km. While the models in Fig. 7.10 give the best fit to the (P-T)Smax conditions, for an initial burial depth of 42 Km, in that the rise in temperature after attainment of (P-T)Smax is low, they require that the heat flux from the mantle was depressed, which is unlikely in an area where rift volcanics were emplaced 30 Ma before thickening. As a result, the models are highly sensitive to variations in heat flux through the lower boundary during metamorphism. Due to the basin activity close to the time of attainment of (P-T)Smax, this heat flux is likely to be enhanced.

Fig.s 7.11 and 7.12 are the results of allowing the initial geothermal gradient to vary from the 10°C per Km modelled in Fig. 7.8. Lowering the initial temperature gradient to 7.5°C per Km results in a slightly later attainment of (P-T)Smax than for the model in Fig. 7.8, but the peak P-T conditions for each trajectory are very similar to those in the latter figure. This result contrasts with that from varying
Fig. 7.8 Class II model with initial temperature gradients of 10°/km:
Fig. 7.9 As Fig. 7.8 but with increased heat flow through the lower boundary: peak temperatures for a given initial depth of burial are at least 50°C higher than for Fig. 7.8.
Fig. 7.10 As Fig. 7.8, but with reduced heat flux through the lower boundary; peak temperatures for a given initial depth of burial are reduced by about 50° C.
Fig. 7.11 As Fig. 7.8 but with depressed initial geothermal gradients of 7.5° C/km:
Fig. 7.12 As Fig. 7.8 but with enhanced initial geothermal gradients of 15 °C/km:
the initial temperature distribution in the class I models, described above, and is due probably to the temperature sink effect of the initially cold wedge of gneiss. The perturbation in the crustal temperature structure that results from this underthrusting is sufficiently great that its re-equilibration effectively swamps the effects of varying the initial temperature distribution. As a result, while both classes of models can produce results that fit with the measured P-T-t histories in the biotite zone, only the class II models allow enhanced initial geotherms, and none of the models allow enhanced heat flux through the lower boundary.

Fig. 7.13 is a set of modelled P-T-t paths for crust in which no low heat producing mafic rocks are present. The conditions are otherwise the same as those in Fig. 7.8. The peak temperatures resulting are about 30°C higher for rock at a given depth of burial than in Fig. 7.8. This model (Fig. 7.13) therefore reproduces the P-T conditions that occurred in the higher grade parts of the biotite zone, to the north-west and the south-east of Tayvallich, and illustrates the important effects of variations in the thicknesses of mafic rock on the P-T-t histories of this area. The increase in grade recorded to the north-west of Tayvallich could therefore be due, to a large extent, to the lower abundance of mafic rock in the crust, with increased depths of burial possibly exerting an additional influence.

7.3.1.3 Class III Models:

The scenario whereby the basement gneiss wedge is emplaced during the D1-D2 deformation is modelled on Fig. 7.14. This model is similar to those of Goffé and co-workers (eg Goffé 1988), and Rubie (1984) except that the cool under-thrust rock is allowed to heat after rapid emplacement instead of being held at a low temperature during a continuous emplacement phase lasting for 10 Ma time-scales. The crust modelled is initially 52 Km thick, the Dalradian making up 42 Km of this thickness. This crust is allowed to heat without uplift, and temperatures of 425°C are attained at depths of 32 to 35 Km after 15 to 20 Ma. Then 10 Km of cooler crust with no internal heat production is thrust rapidly between the Dalradian and the crustal basement, this under-thrust crust representing the basement gneiss wedge. The crust then undergoes uplift at 0.3 Km per Ma, again similar to the uplift rates in the other models. Two models have been produced, the initial temperatures in the gneiss wedge ranging between 100 and 180°C, and between 260 and 340°C.

In both models, cooling in the Dalradian is rapid for ca. 10 Ma, then the rock
Fig. 7.13 As Fig. 7.8 but with the low heat producing layer within the Dalradian removed and replaced by rocks with higher heat production rates:
Fig. 7.14 $P$-$T$-$t$ paths from the class III models for the biotite zone: primary metamorphic $P$-$T$ conditions are attained within 20 Ma of initial thickening, and ($P-T_{S_{\text{max}}}$) temperatures are the highest attained; increasing the temperature of the gneiss wedge does not alter the shape of the paths significantly.
packet initially buried at 34 Km starts to heat slowly. In the model with the
cooler wedge, the rock packet never exceeds 400°C, while in the model with the
warmer wedge, the rock packet buried at 34 km rises in temperature further, but
never exceeds the temperature at the time of under-thrusting. The class III models
are therefore relatively insensitive to variations in the temperature of the
under-thrust wedge.

The rocks buried initially at 32 to 35 Km spend at least 70 Ma at temperatures
between 350 and 400°C, cooling through 375°C at 465 Ma ago (70 Ma after
under-thrusting) and through 325 °C 20 Ma later. Thus, the P-T-t history from
this model reproduces the measured P-T-t constraints closely, with the added
advantages that the (P-T)_{S_{max}} conditions are attained sooner after thickening
than with the other models, and that the temperatures at S_{max} are the highest
attained by each rock packet.

7.3.1.4 Summary of Models for the Biotite Zone:

All the models of biotite zone metamorphism were derived using parameter
ranges imposed as far as possible by measurements made on natural samples.
Most of these models result in P-T-t trajectories that pass through the (P-T)_{S_{max}}
conditions, indicating that the parameter ranges and values are consistent. As a
result, there is no unique model for regional metamorphism in the biotite zone.
However, the models all indicate that the high pressure, low temperature
metamorphic conditions will result if heat production rates are low (as argued by
Graham 1986). In addition, the slow rates of uplift and cooling also help preserve
the high pressures, because increasing the rate of uplift results in advection of
heat towards the surface, and temperatures increasing further during uplift. Slow
uplift, combined with low rates of heat production, but with values within the
ranges of measurement are therefore able to produce low-temperature,
high-pressure metamorphism.

In all the models presented, the P-T-t trajectories pass through 10 Kbar and
425°C while the rock packet concerned is heating. In all cases, except for very
low heat fluxes through the lower boundary, and for the class III models, heating
of the rock packet continues for some time after the P-T-t trajectory passes
through the (P-T)_{S_{max}} conditions. The P-T-t trajectories usually pass through this
point in P-T space about 35 Ma after the initial thickening episode invoked for
these models, but pass through this point in P-T space within 20 Ma of initial
thickening in the class III models. As a result of the slow rates of cooling and uplift, the rocks passing through \((P-T)_{S_{\text{max}}}\) spend up to 70 Ma at temperatures in excess of 375°C in all the models, giving ample opportunity for re-equilibration in mineral assemblages and isotopic systems, subsequent to the attainment of \((P-T)_{S_{\text{max}}}\). This observation may be able to explain the scatter in the Rb-Sr age data in phengites in these rocks (chapter 6).

Though all the models produce P-T-t paths that pass through \((P-T)_{S_{\text{max}}}\) conditions, the class II and class III models, which involve cool crust at depth at some time in the modelled thermal history, are more robust to variations in the starting and running conditions, with the class II models able to accommodate changes in initial temperature distributions, and the class III models allowing the thickening and primary metamorphism to occur closer together in time than the other models. Thus, the class III models allow any enhanced lower boundary heat flux, or geothermal gradient, that may have resulted from sedimentary basin activity, to relax further prior to regional metamorphism. As has already been stressed, none of the models presented provide a unique reproduction of the regional metamorphism in the biotite zone, but the models with cool rock at deep levels in the crust are more robust to variations in the starting conditions, especially resulting from sedimentary basin activity. The presence of such cool, low heat producing crust at depth is therefore likely to have been instrumental in preserving the P-T conditions of metamorphism observed.

### 7.3.2 Thermal Models of Metamorphism in Knapdale:

The \((P-T)_{S_{\text{max}}}\) conditions of metamorphism in the garnet zone are about 500 to 550°C and 10 to 11 Kbar. The crust also has a lower proportion of low heat production rate rock compared with the crust in the biotite zone, with less mafic rock, and a thinner wedge of basement gneiss separating the Dalradian sequence from the crustal basement. However, due to the syn-depositional igneous activity, the initial temperature distribution, and heat flux through the lower boundary is still problematical. Because the mafic rocks are distributed homogeneously in the garnet zone on the scale of resolution of the models, the Dalradian crust is treated as having a homogeneous radiogenic heat production rate. Models for heat production rates of 2.0, 2.2, 2.3, and 2.5 HGU were made, encompassing the probable range in these parameters (table 7.1), but still low in comparison with the mean heat production rates calculated by Richardson and Powell (1976) as...
being about 4 HGU.

The models created include some which assume steady rates of uplift throughout the rocks' P-T-t histories, and others with transient, rapid, uplift, to simulate the possible thermal effects of nappe emplacement. The effects of nappe emplacement, involving major horizontal movement with possible advection of heat, can only be modelled properly by a two-dimensional thermal model, which is beyond the scope of this thesis. In addition, significant lateral heat transfer may have occurred during primary metamorphism. Thus, the models of garnet zone metamorphism can only be approximate.

### 7.3.2.1 Class I and Class II Models With Steady Uplift Rates:

Five model P-T-t paths are shown on Fig. 7.15, for heat production rates of 2.0, 2.3 and 2.5 HGU, the paths starting at initial burial depths of 38 and 40 Km, and with erosion at 0.3 Km per Ma starting 20 Ma after burial and thickening. While the models for Tayvallich assume that uplift slows at about 40 Ma after thickening, the models for the garnet zone assume constant uplift throughout, in order to account for the necessarily quicker uplift in the garnet zone (7.2.3.4).

In all three steady uplift rate models, the paths pass through P-T conditions close to (P-T)$_{S_{max}}$, but reach higher temperatures at subsequent stages in the rocks' P-T-t histories, reaching peak temperatures of between 525 and 575 deg. C at 8 to 9 Kbar (30 Km depth). The paths pass through (P-T)$_{S_{max}}$ between 30 and 40 Ma after initial thickening. The textures and fabrics throughout Knapdale and Tayvallich indicate that primary metamorphism in the biotite and garnet zones occurred at about the same time, since the $D_1$-$D_2$ deformation is unlikely to have been diachronous to any great extent. The models therefore give consistent results by use of starting and running conditions and parameters estimated from measurements made on similar rock types. The models indicate that a combination of a greater depth of burial and higher heat production rates are needed to produce the higher temperatures of metamorphism in the garnet zone, assuming that the comparative rates of uplift in the biotite and garnet zones are as modelled.

The P-T-t paths generated by these models are very similar to those produced by the class I and class II models for the biotite zone, especially with respect to the time of attainment of the (P-T)$_{S_{max}}$ conditions, and the post-(P-T)$_{S_{max}}$
Fig. 7.15 Class II model P-T-t paths for the garnet zone of South Knapdale: paths correspond to homogeneously distributed heat production rates of 2.0, 2.3, and 2.5 HGU in the Dalradian crust.
behaviour. In the garnet zone, metamorphism was accompanied by nappe emplacement which may have caused transient, rapid cooling as a result of the horizontal advection of heat. Since the model used in this chapter is 1-dimensional, it cannot simulate this kind of thermal history accurately, but models with a short period of rapid uplift were made to see if the P-T-t paths can be made to start their cooling phases earlier. These are described below.

7.3.2.2 Class II Models With Varying Uplift Rates:

The model P-T-t paths for crust with a steady uplift rate reach (P-T)Smax at between 30 and 40 Ma after burial and thickening. As a result, models assuming uplift rates of 2 Km per Ma at 30, and 40 Ma after burial were made for the three heat production rates used in the steady uplift rate models; the results are shown on Figs 7.16 and 7.17. In all cases, the peak temperatures reached are very similar to those reached by the constant uplift rate models, but with given points on each P-T-t path reached about 10 Ma sooner after thickening. Thus, the main effect of the rapid uplift pulse is to accelerate the P-T-t history marginally, without affecting the shape of the P-T-t path radically; the rocks cannot be forced into cooling immediately after (P-T)Smax by a short period of rapid uplift.

A model assuming a heat production rate of 2.2 HGU and initial temperature gradients of 15°C per Km is shown on Fig. 7.18, with rapid uplift at 30 Ma after burial. The P-T-t path is very similar to that produced by crust with a heat production rate of 2.5 HGU and initial temperature gradients of 10°C per Km, but the (P-T)Smax conditions are reached about 5 Ma earlier than for the other models with less enhanced initial geotherms. This is simply because the rocks do not need to rise in temperature so far before reaching the (P-T)Smax conditions.

7.3.2.3 Class III Models:

A scenario that involved the under-thrusting of a wedge of cool, low heat producing gneiss after the initial thickening and burial event was particularly effective in preventing the biotite zone models from recording increasing temperatures subsequent to attainment of (P-T)Smax. Such a scenario is less likely to be effective in forcing the garnet zone into cooling after attainment of (P-T)Smax because the gneiss wedge is thinner beneath South Knapdale, and the heat production rates and temperatures in the over-riding (Dalradian) crust are both higher. However, results from class III models produced in a similar manner
Fig 7.16 As Fig. 7.15, but with rapid uplift after 30 Ma: the peak temperatures are very similar to those in Fig. 7.15, but are attained about 10 Ma earlier.
**Fig. 7.17** As Fig. 7.15, but with rapid uplift at 40 Ma:
Fig. 7.18 Model P-T-t path for Dalradian crust with a heat production rate of 2.2 HGU, initial temperature gradients of 15° C/km, and rapid uplift after 30 Ma; Ma; primary metamorphic P-T conditions are attained within 25 Ma of burial.
to the class III models for the biotite zone, are shown in Fig. 7.19, for temperatures in the gneiss wedge of 100 to 140 and 150 to 180°C.

The shapes of the P-T-t paths produced in these models are similar to those produced by the biotite zone models, with rapid cooling followed by slow heating. However, due presumably to increased heat production rates and a thinner cool gneiss wedge, the slow heating phase results in similar peak temperatures to those produced in the other models for the garnet zone already discussed. As with the late under-thrusting models for the biotite zone, (P-T)_{Smax} conditions are reached within 20 Ma of thickening, but in the case modelled here, post Smax temperatures for each P-T-t trajectory are significantly higher. It is therefore very difficult, within the slow cooling rates imposed by the information available, to prevent rocks in the garnet zone from reaching higher temperatures than those preserved in the primary assemblages during post D_1-D_2 uplift.

The late under-thrusting models in both garnet and biotite zones allow more rapid heating phases in each of the P-T-t trajectories produced. This is because the gneiss wedge, being cold and having low heat production rates acts as a heat sink if present at the beginning of orogenesis. Its absence during the first 15 to 20 Ma of heating allows more rapid heating in the Dalradian crust, especially at deeper levels.

7.3.2.4 Summary of Models For Garnet Zone Regional Metamorphism:

The models for garnet zone metamorphism produce P-T-t paths that are very similar to the P-T-t paths produced by the equivalent models for the biotite zone metamorphism. Class I and class II models all attain P-T_{Smax} conditions about 35 Ma after initial thickening, as well as suggesting that a given rock packet continues to rise in temperature subsequent to the attainment of (P-T)_{Smax}. Both sets of models also suggest that each rock packet stays at temperatures within 50°C of the highest temperatures attained for at least 50 Ma. Given that the uplift rates used for both biotite and garnet zone models are similar, the similarity in the results is perhaps hardly surprising, but both sets of models produce P-T-t trajectories that are mutually consistent. The parameter ranges used in these models, estimated from measurements on "real" rocks, are therefore also mutually consistent.

It is clear, however, that the garnet zone models are less sensitive to changes in
Fig. 7.19 Class III model $P$-$T$-$t$ paths with Dalradian crust heat production rates of 2.5 HGU: primary metamorphic $P$-$T$ conditions are attained about 20 Ma after initial thickening.
uplift rates and temperature profiles than the biotite zone models. In addition, the garnet zone models predict that the temperatures recorded in the primary assemblages are not the maximum temperatures experienced by the rocks, but that the maximum temperatures were experienced after the primary metamorphism. This prediction rests on there being no significant horizontal heat transfer which may cause the garnet zone to cool down after attainment of \((P-T)_{S_{\text{max}}}\). In view of the suggestions made in 5.4.3, and chapter 6, that cooling rates were certainly slow, and that the rocks now on the surface may well have continued heating after \((P-T)_{S_{\text{max}}}\), this prediction of the model is consistent. Alternatively, horizontal heat transfer may also result in more rapid heat loss from the garnet zone (below, 7.4.1).

As with the biotite zone models, most of the garnet zone models will reproduce the measured P-T-t histories closely, despite varying the input and running conditions. There is therefore no unique model for the garnet zone metamorphism. However, the late under-thrusting models, by allowing a relatively rapid heating phase followed by more controlled post \(S_{\text{max}}\) heating answer many problems associated with the models that need a longer heating phase. These problems are discussed further in section 7.4.

### 7.3.3 Thermal Models of Metamorphism in Northern Kintyre:

The regional metamorphic history of Northern Kintyre is much more complex than that of Knapdale and Tayvallich, due primarily to pervasive over-printing deformation. The early secondary assemblages show evidence of growing under high temperature conditions. The models will need to produce elevated temperatures at 30 km depths in the crust for long periods of time. In addition, the models need to suggest that cooling through given temperatures occurred later than in Knapdale and Tayvallich.

None of the basement gneiss under-thrust from the north-west is likely to be present in Northern Kintyre, based on the deep seismic reflection data (Fig. 7.4). In addition, there is little mafic rock in the Dalradian crust in Northern Kintyre, and the Dalradian crust at present is also thicker than in Knapdale (Fig. 7.4). Thus, a smaller proportion of the crust present during regional metamorphism was made up of rock with low heat production rates, suggesting in turn that peak temperatures should be higher. P-T conditions are less well constrained in
**Fig. 7.20** Model $P$-$T$-$t$ paths for Northern Kintyre with heat production rates of 2.5 HGU; one path is for steady uplift rates while the other is for rapid uplift at 30 Ma: primary metamorphic $P$-$T$ conditions are attained within 25 Ma of burial.
Northern Kintyre than in Knapdale, but pressures of 11 to 12 kbar from relict primary metamorphic assemblages suggest deeper initial depths of burial than in Knapdale and Tayvallich.

Model P-T-t paths are shown on Fig. 7.20 for constant rates of uplift at 0.3 km per Ma, and for a pulse of rapid uplift (2 km per Ma) at 30 Ma after thickening. The main features of these paths are identical to the early under-thrusting models for the garnet zone, with peak temperatures reached at depths of about 30 km for rock initially buried at 40 km, about 55 Ma after burial for the constant uplift rate model, and about 45 Ma for the varying uplift rate model. Between 20 and 30 Ma, the rock initially buried at 40 to 42 km passes through P-T conditions of 11 to 12 kbar (35 to 38 km) and about 550°C, the estimated P-T conditions during D1-D2 deformation.

The rock buried initially at 40 km reaches a peak temperature of about 615 deg. C, about 30°C higher than the 2.5 HGU early under-thrusting model for South Knapdale, despite the uplift rates used in the two models being equal. The differences between the peak temperatures produced by the two models is probably due to a combination of two factors: the lower proportion of low heat production crust, and the absence of the gneiss wedge beneath the Dalradian crust in the Northern Kintyre models. The estimated P-T conditions during D1-D2 deformation are also attained more rapidly, within 25 Ma of initial thickening, than the class I and class II models for South Knapdale, again probably due to the absence of the gneiss wedge under Northern Kintyre. As a result, the timing of heating and cooling suggested by the Northern Kintyre models is more consistent with the class III models for South Knapdale.

The models indicate that the highest temperatures were attained about 30 Ma after the passage through the P-T conditions of the primary metamorphism and the D1-D2 deformation. Remembering that the geochronological data in chapter 6 suggest that the early secondary metamorphism occurred up to 35 Ma later than the primary metamorphism, the models for Northern Kintyre are consistent with the suggestion that the rocks were still hot during the early secondary metamorphism, and predict that the early secondary metamorphism may have occurred close to the highest temperatures attained in the rocks now present on the surface. The parallels between Northern Kintyre and the Central Highlands are clear (eg Dempster 1985).
However, the early under-thrusting models for the garnet zone also show post-D\textsubscript{1}-D\textsubscript{2} heating, which was ascribed to the inability of the models to account for possible horizontal heat transfer. Clearly, similar phenomena may have occurred in Northern Kintyre with possible horizontal heat transfer towards the Highland Border (cf. Harte and Dempster 1987) as well as to the north-west. Thus, like the garnet zone models, the Northern Kintyre models should be interpreted with care. It is clear, though, that the Northern Kintyre models suggest strongly that the deep crust was at elevated temperatures for 50 Ma or more, consistent with the suggestion of the rocks' being hot during the early secondary deformation and metamorphism.

It is clear that, in a given vertical column of rock being modelled, rock buried initially deeper will cool through a given temperature later than a rock buried at a more shallow level. As a result, the deeper initial burial of the rock in Northern Kintyre than in South Knapdale will contribute to the lowering of cooling ages in Northern Kintyre. However, at an uplift rate of 0.3 km per Ma, rock buried 3 km (approx. 1 kbar) deeper will cool through a given temperature about 10 Ma later than the rock at a shallower level. As a result, the rate of uplift in the Northern Kintyre area needs to have slowed relative to that in Knapdale at some stage in the cooling history, since the difference in the lower closure temperature cooling ages is up to 30 Ma. The difference in uplift rate would presumably have come about during the steepening of the root of the Tay Nappe, now forming the Knapdale steep belt.

The absence of ca. 400 Ma old granite plutons in the South West Highlands has been noted (eg Graham 1986), and it has been speculated that the crustal basement in the South West Highlands is refractory and dense. In addition, it was also suggested by Graham (1986) that the deeper levels of the crust would not reach high enough temperatures to cause melting. The thermal models presented in this chapter indicate that the lower levels of the crust reach maximum temperatures of about 700 to 800ºC. In addition, the geophysical evidence indicates that the lower and middle crust in the South West Highlands is refractory, either being dense, therefore mafic, or being gneissic. Thus, though the minimum melting temperature of granite of about 700ºC has probably been exceeded, melting is unlikely to have occurred on the scales needed to produce the volumes of granite seen in the rest of the Scottish Dalradian. In addition, A.B. Thompson (1986) shows that several rock-volumes of fluid are needed to
produce one rock-volume of granite. Such fluid abundances are unlikely in the refractory and gneissic rocks in the deep crust in the South West Highlands.

### 7.4 Conclusions and Implications of the Thermal Models:

To re-iterate the aims of this chapter, the thermal modelling had the aim specifically of indicating the ways and mechanisms whereby high-pressure, low-temperature metamorphic assemblages developed on a regional scale could be preserved in crust that cooled slowly after the attainment of the highest temperatures.

The starting and running parameters used in the models were estimated as far as possible from measurements made on rocks from the area, or in the case of Richardson and Powell (1976), on very similar rocks. The resulting modelled P-T-t trajectories mimic closely the P-T-t histories derived by the geochronological and petrological data gathered in this study. Thus, the contrasts in the starting and running conditions of the models for each of the three areas examined are consistent with the observed differences in P-T conditions and the metamorphic histories.

Essentially, the models presented in this chapter are of two types: those which assume that a wedge of high-grade gneiss was emplaced at the beginning of orogenesis, the early under-thrusting models, and those models which suggest that the gneiss wedge was emplaced beneath the Dalradian at the time of the primary deformation and metamorphism, the late under-thrusting models.

If the models are an accurate reflection of metamorphic processes in the South West Highlands, there are four major conclusions to be drawn which need further discussion and amplification. These conclusions are as follows:

1. the temperatures and pressures preserved by the primary assemblages are attainable, despite uplift and cooling rates being low, with heat production rates in the models that are similar to those measured in similar lithologies. The models therefore show that the P-T conditions that have been measured are attainable in a metamorphic belt that has undergone slow uplift. The main reason for the preservation of the P-T conditions of metamorphism that have been measured is that the heat production rates in the Dalradian crust in the South West Highlands were low. However, most of the modelled P-T-t paths record increased temperatures subsequently to the attainment of the P-T conditions of the primary metamorphism.
2. The primary assemblages are preserved mainly as a result of the absence of secondary deformation: the models implying that temperatures at the time of the secondary metamorphism may have been higher in some areas (eg Northern Kintyre) than during the primary metamorphism.

3. The duration of the heating phase required by the models varies between 15 and 35 Ma, according to the time of emplacement of the basement gneiss wedge exposed in Western Islay. The duration of the heating phase therefore places constraints on when Dalradian deposition could have ceased. However, both early and late under-thrusting models produce cooling paths that are consistent with observation. Because the ending of Dalradian deposition is not well constrained, a choice between the two types of models is difficult.

4. The models produced in this chapter are not immediately consistent with those of Dempster (1984, 1985) who suggested that $D_1$-$D_2$ deformation represented the time of initial thickening of the Dalradian crust in thermal models of metamorphism in the Central Highlands. The heat production rates in the South West Highlands are required to be low, otherwise the temperatures in the crust will rise too far. As a result, relatively long heating times are required which need to start prior to the $D_1$-$D_2$ deformation, since this was when primary metamorphism occurred (section 3.4).

Each of these conclusions will now be discussed more fully in turn.

7.4.1 Were the Temperatures of Primary Metamorphism the Highest Recorded?:

The discussion in this subsection pertains mainly to the first two of the four conclusions listed above. The models showed that the primary P-T conditions were attainable by the models, but that it is very difficult to prevent subsequent heating by up to $50^\circ$C above the recorded temperatures of primary metamorphism, the only exception being the class III models for the biotite zone. The problem therefore reduces to one of whether the one-dimensional models used in this chapter are accurate, that is, if heat transfer takes place only by conduction, and only in a vertical direction.

It has been estimated in 7.2.1 above that the rate of horizontal heat transfer during the primary metamorphism was no more than 20% of the rate of vertical heat transfer, as a result of the temperature differences between the biotite zone and the garnet zone at this time. However, if the rocks were flat-lying to inclined during the primary metamorphism, the alignment of the schistosity, hence of the maximum conductivity (eg Wenk and Wenk 1973, Richardson and Powell 1976),
would lie in this direction, thus increasing the rate of horizontal heat transfer. Based on the conductive anisotropy measurements cited above, the rate of heat transfer horizontally could be as much as 40% of that of the vertical heat transfer. Therefore, the rate of cooling in the garnet zone could easily be enhanced to the extent that the rocks start to cool at greater depths than predicted by the models in this chapter. Ridley (1988, in press) shows that such enhanced cooling, without radically altering the shape of the P-T-t paths, will occur in crust where the rate of horizontal heat transfer is significant.

The other possible means of enhancing cooling rates is the advection of heat by fluid flow. Graham et al. (1983) showed that fluid/rock ratios were locally very high during the primary metamorphism (see also chapter 3), and Bickle and McKenzie (1987) have shown that fluid with a fast enough flow rate will advect heat. This possibility is less well constrained than the possibility for horizontal heat transfer, though Greig (1985) used non-equilibrium thermodynamics to calculate flow rates at South Bay during the primary metamorphism; these flow rates were fast. However, if fluid flow rates were fast, the fluid infiltration event would be transient, resulting in a short time-scale thermal structure which might then be swamped by subsequent thermal relaxation. Thus, the cooling as a result of advective heat transfer by fluids might well be brief, and not significant over the longer time-scales of these models.

If either, or both, of the alternatives to one-dimensional conductive heat transfer were significant during the primary metamorphism, the garnet zone would cool more rapidly than predicted by the models while the biotite zone would cool more slowly. The late under-thrusting models for the biotite zone suggest that the primary metamorphic temperatures are the highest recorded in this area; the biotite zone can therefore cool more slowly than predicted by this model and still be consistent with observation.

If the one-dimensional models are reasonable representations of geological reality, they have three major implications:

1. the presence of high temperatures in the garnet zone was not sufficient in itself to cause secondary metamorphism; metamorphism occurred only as a response to pervasive deformation, which occurred only during D1-D2 times in the garnet zone. As a result, the preservation of high-pressure, low to medium-temperature assemblages was due mainly to the absence of post D1-D2 pervasive deformation. In contrast, Northern Kintyre did experience major post D1-D2 deformation, so secondary assemblages resulted.
2. The one-dimensional thermal models predict that the garnet zones of South Knapdale, and Northern Kintyre, reached their highest temperatures at about the time of the early stages of the secondary deformation. Since this deformation was equivalent to the D$_3$ deformation in the Central Highlands, the parallels with the Central Highlands are obvious, with the highest temperatures occurring in both areas simultaneously.

3. The prediction that the garnet zones remained at temperatures above 500°C for up to 50 Ma after primary metamorphism is clearly consistent with observations implying that South Knapdale and Northern Kintyre either cooled very slowly, or continued heating, after D$_1$D$_2$ deformation. Thus, the reset garnet zoning and polyphase garnet growth, along with scattered Rb-Sr ages in phengites, both resulting from kinetic processes with closure temperatures of ca. 500°C at cooling rates of less than 10°C Ma$^{-1}$, are consistent with the models' suggesting that the upper garnet zone, and the Northern Kintyre crust, remaining at temperatures greater than 500°C for long periods of time after the primary metamorphism.

Though there is not enough information available to constrain the above speculations more closely, the arguments for significant horizontal heat transfer outlined above suggest that the models may not reproduce the early cooling history of the garnet zone very accurately. As a result, cooling after D$_1$-D$_2$ deformation is inferred. However, the independent petrological and geochronological evidence for high temperatures for long periods of time after primary deformation and metamorphism imply that horizontal heat transfer may not necessarily have been significant, and that, given the constraints available, the one-dimensional models predict and reproduce the early heating and cooling histories of the higher grade areas accurately.

The probability that temperatures throughout the South West Highlands remained high after D$_1$-D$_2$ deformation still indicates strongly that deformation was needed to produce regional metamorphic assemblages in the South West Highlands. Northern Kintyre underwent slower cooling from higher temperatures, and the highest temperatures may still have been above those present during D$_1$-D$_2$ deformation, so this area was obviously the most susceptible to deformation and overprinting metamorphism. In view of the various models of porphyroblast growth reviewed in chapter 4, the conclusions of this paragraph should not be surprising.
7.4.2 When Did Caledonian Orogenesis Start?:

The discussion in this subsection concerns the second two of the four conclusions listed at the beginning of this section. The models predict that between 15 and 35 Ma are needed for the heating phase prior to the primary metamorphism. The initial thickening event necessary to trigger Dalradian regional metamorphism is therefore constrained to have occurred at between 540 and 560 Ma ago, assuming that the oldest Rb-Sr phengite age measured (524±5 Ma) is close to the time of primary metamorphism. The predicted timing of the start of Caledonian orogenesis (the timing of the initial thickening episode), depends very strongly on the class of model, hence the time of emplacement of the basement gneiss wedge. The class III (late under-thrusting) models requiring a short (15 to 20 Ma) pre-primary metamorphism heating phase.

In 7.2.3, the role and the timing of the emplacement of the basement gneiss wedge was discussed. There were two alternatives, neither of which could be ruled out due to lack of clear constraint. Either the basement gneiss wedge was emplaced at the beginning of Caledonian orogenesis, and was therefore likely to have been during the initial thickening episode, and the West Islay Shear Belt formed as a result of re-activation of the contact between the gneiss wedge and the Dalradian, or the basement gneiss wedge was emplaced during the primary deformation and was therefore likely to be the cause of the nucleation and propagation of the Tay Nappe. The models described in this chapter could therefore be a test between these two alternatives.

It is clear from the discussions of the results of the various models that the class III models are less sensitive to variations in enhanced heat flux through the lower boundary as a result of Dalradian sedimentary basin activity, simply because these models allow more time to elapse between the ending of the basin activity and the initial crustal thickening episode, thus making it more likely that basin activity had ceased to be a significant source of heat at the time of the initial burial. The class I and class II models will be more sensitive to basin activity, because the required time for burial is probably within 35 Ma of the earliest possible time for the cessation of Dalradian deposition, while the class III models allow up to 60 Ma to pass.

The models which assume that the gneiss wedge was cool (the class II and
class III models) on emplacement are also more robust to variations in initial
temperature gradients and heat flux through the lower boundary than the models
which assume that the gneiss wedge was warm on emplacement (class I models).
This is because the cool gneiss wedge acts as a heat sink in the models, thus
preventing temperatures from rising too far after burial. As a result, though the
class I models can reproduce (P-T)_{Smax} conditions, the starting and running
conditions necessary to do this cannot vary to the extent permitted by the class II
and class III models. Thus, the models suggest strongly, but do not prove, that the
gneiss wedge was cool on emplacement, and are therefore consistent with the pre
600 Ma timing of the pre-\(D_1-D_2\) deformation seen on West Islay and Colonsay
(section 7.3.2).

For all of the reasons just outlined, the class III models, which infer a syn
\(D_1-D_2\) emplacement of the basement gneiss wedge are better at reproducing the
measured P-T-t histories throughout the South West Highlands than the other
models, are less sensitive to possible, but unconstrained, variations in the starting
and running conditions, and are more consistent with the available constraints on
the pre-\(D_1-D_2\) tectono-metamorphic history of the region. The modelling
therefore indicates, but does not prove, that Caledonian Orogenesis started about
540 to 545 Ma ago.

The major implication of this conclusion is that the emplacement of the
basement gneiss wedge, as speculated in 7.3.2, and corroborated by the
information on the structures in the region derived in other studies, occurred
during \(D_1-D_2\) deformation, and was therefore the cause of the nucleation and
emplacement of the Tay Nappe, at least in the South West Highlands. The Tay
Nappe also formed at great depth and is therefore more likely to have formed in
the manner described in section 2.5 than as a result of shallow-level gravity
sliding, as has often been advocated (eg Roberts 1974, Shackleton 1979, Anderton
1988). This implication is therefore of profound regional importance, since it
provides a mechanism in plate tectonic terms for the dominant structures in the
Scottish Caledonides, this explanation being entirely consistent with the available
constraints on the timing of Caledonian orogenic activity (cf. Dewey and
Shackleton 1984).

The other major implication of the models of this chapter is that a tectonic
event occurring at ca. 540 to 545 Ma ago is inferred by the models. To my
knowledge, no evidence for any such episode has been found yet in the
Caledonide-Appalachian chain in the North Atlantic region, but it is difficult to see how such an episode can be avoided, if the necessary low heat production rates, and hence, slow rates of temperature change in the thickened crust are to be accepted as having occurred.

The models presented in this chapter are consistent with the models produced by Dempster (1984, 1985) for the Central Highlands. Dempster (1984, 1985) suggested that the initial thickening in the Dalradian occurred at ca. 540 Ma, but inferred this as being during the \( D_1 - D_2 \) deformation, rather than before hand as suggested here. This suggestion is shown in this thesis to be unnecessary in Dempster's models, since a pre-\( D_1 - D_2 \) thickening event, occurring within 5 to 10 Ma of the time of thickening inferred by Dempster's models, has been shown to be consistent with the measured P-T-t histories in the South West Highlands. The suggestion that the initial thickening episodes occurred at similar times throughout the Scottish Dalradian suggests that the differences in the metamorphic histories between the Central, and the South West Highlands are due mainly to local differences in crustal composition and heat production rates, not to local differences in the tectonic histories prior to the \( D_1 - D_2 \) deformation. The testing of this conclusion, which was argued for by Graham (1986) was one of the main aims of this thesis, and will be discussed further below.

7.5 Controls on Regional Metamorphism in the South West Highlands:

The contrasts in the models for regional metamorphism in the Central Highlands and the South West Highlands itemised above illustrate the contrasts in the controlling factors of regional metamorphism that were in force in the two areas. In the Central Highlands, the Dalradian is underlain by a large thickness of metasedimentary rock that probably had a high rate of heat production, inferred to be about 4 HGU by various thermal models of the region (Richardson and Powell 1976, Wells 1979, Dempster 1985). The underlying metasediments (exposed on the surface as the Grampian Division (Dalradian) and Central Highland Division (Moine)) would be an equivalent in the Central Highlands to the basement gneiss wedge in the South West Highlands with respect to the large scale crustal structure. The models in this chapter illustrate the importance of the gneiss wedge in reducing the peak temperatures in the overlying crust by acting as a heat sink. As was shown by Wells (1979), the underlying metasediments in the Central Highlands acts as a heat source resulting in the higher temperatures of
metamorphism in this area.

The presence of large volumes of mafic rock in the South West Highlands has also been shown by the models to be significant. In Tayvallich, mafic rock made up at least 10% of the thickened crust being modelled, and makes up about 30% of the present-day thickness of the Dalradian in the South West Highlands. Removing this rock from the biotite zone models results in peak temperatures increasing by about 30 °C. One of the reasons for the strong influence of the mafic rock would be the fact that it was present at depth in the models. Putting higher heat production rate crust on the surface in the models as a starting condition will not be as influential as putting the same thickness of crust with the same thermal properties at depth, because the surface crust is eroded rapidly, and the heat build-up is less due to the upper boundary being closer; the length-scales of heat transfer are less so the time-scales of heat transfer are reduced. The presence of mafic rock at depth results in the low heat production rates being present in the crust throughout the running time of the models. As a result, despite being relatively localised, and making up a relatively small proportion of the crust at the time of thickening, the mafic rocks have resulted in a lowering of metamorphic grades in the regions where they are concentrated.

As a result, the models show that the main control on metamorphic grade in the South West Highlands was the composition of the crust undergoing metamorphism. Contrasts in crustal composition on both small and large scales were significant, with the thickness of the basement gneiss wedge beneath the Dalradian, and the proportion of mafic rock within the Dalradian, being the two most important influences on metamorphic grade. The other major, but less well constrained, influences on metamorphic history are the possible variations in starting and running conditions discussed throughout this chapter and concluded in this section. Thus, the heating rate of the thickened crust depends on the tectonic history of the Dalradian, while the highest temperatures attained depend on the influence of factors other than one-dimensional heat transfer by conduction on the cooling rates of the metamorphosed pile.

The models therefore show that the measured P-T conditions and the timing of heating and cooling rates are consistent with what is known about the crustal structure and composition in the South West Highlands. The study is now essentially complete; the next chapter is designed to synthesise the conclusions of this study, and to place them in the wider context of regional metamorphism in
the Dalradian as a whole, as well as to illustrate the potential importance of this integrated case study of regional metamorphism for other studies of metamorphic belts.
CHAPTER 8
CONCLUSIONS, IMPLICATIONS AND OUTSTANDING PROBLEMS:

"We shall not cease from exploration
And the end of all our exploring
Shall be to arrive where we started
And to know the place for the first time."

T.S. Eliot, Little Gidding

The results of the studies described in this thesis are significant, both for the orogenic history of the Scottish Dalradian, and for our understanding of the processes of regional metamorphism and related tectonic activity as a whole. Many of the results of this study will also prove to be significant for our understanding of the kinetic behaviour of elemental and isotopic systems in common pelitic minerals. The major point of significance for understanding of Dalradian orogenic processes is the preservation of the early stages in these processes in a region with a relatively simple structural and metamorphic history. For regional metamorphic processes in general, the most significant conclusion of this study is the illustration of the role of contrasting lithologies and crustal composition in the formation of differing metamorphic facies, which has resulted in the preservation of high-pressure, low- to medium- temperature mineral assemblages as the dominant mineralogy in region which has undergone slow cooling and uplift. In this chapter, these major implications will be discussed further, and it will be shown how they are inter-related and hence that the Dalradian metamorphic belt as a whole is a particularly good example of the controls on regional metamorphic evolution.

8.1 Implications for Dalradian Orogenic Evolution:

Much of this thesis is concerned with the comparison between the metamorphic evolution of the South West Highlands of Scotland and that of the rest of the Scottish Dalradian. The latter region has therefore tended to be taken as having a distinct tectono-metamorphic history, but the major contrasts within have not been emphasised. This is a major oversimplification; the Dalradian of the Central, Southern and Eastern Scottish Highlands shows many major contrasts
and variations in its sedimentological, structural, and metamorphic evolution (Fettes et al. 1986 Harte 1988). However, the main contrast between the South West Highlands and the rest of the Scottish Dalradian is in the preservation of an early stage in the metamorphic history of the South West Highlands, and in the relative simplicity of this history. Essentially, the dominant metamorphic assemblages in the South West Highlands grew relatively early in the structural history of the region, this early growth being supported by the geochronological evidence, and the assemblages formed are relatively low grade. In contrast, though there are many complications (eg Dempster and Harte 1986), the assemblages in the rest of the Scottish Dalradian grew later in the deformational history, and are usually higher grade, often being metamorphosed under lower pressures.

The Scottish Dalradian as a whole can be divided into a number of provinces, each of which has distinct characteristics with respect to its pre-metamorphic, and metamorphic histories (Harte 1988). These provinces are separated by lineaments (Fettes et al. 1986) that are inferred from the geology, but often observed and defined from the geophysics. Of these lineaments, the Cruachan Lineament is probably one of the more important; the South West Highlands is, as a result, one of the larger of these provinces. Several of these provinces are present in the region north-east of the Cruachan Lineament and south-west of the Portsoy-Duchray Hill lineament (see also section 2.3); it is this broad area with which the majority of the comparisons with the South West Highlands have been drawn in this thesis.

8.1.1 Contrasts in the Crustal Structure:

Taking the Central Highlands as a region, once again, the major distinction between the Central Highlands and the South West Highlands is in the crustal structure. The Central Highlands consists of Dalradian rocks on top of Central Highland Division rocks, lying in turn on crustal basement of unknown lithology and composition. In contrast, the South West Highlands consists of Dalradian rocks of Appin Group age and younger resting on a thin sequence of sediments resting in turn on high grade gneiss which in turn lies on top of a mafic crustal basement. As a result, the average heat production rates in the crust in the Central Highlands are higher than those in the South West Highlands, leading in turn to higher grades of metamorphism. It is almost certainly no accident that the Central and Eastern Highlands has had a far more complex structural history than

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the South West Highlands as a direct result of the crust in the former area reaching higher peak temperatures during its orogenic history. The more complex structural history in the Central and Eastern Highlands has presumably lead in turn to the more complex metamorphic evolution of the region, since metamorphism, uplift rates, and deformation are often very closely linked (eg Dempster 1984, 1985, Dempster and Harte 1986).

The main question to be asked therefore, is: how did the differences in the crustal structures between the various Dalradian provinces come about? In the Central Highlands, Appin Group and younger rocks are emplaced along south-eastward dipping tectonic contacts over older rocks, in this case the Grampian and Central Highland Division. In the South West Highlands, Appin Group and younger rocks are emplaced along south-eastward dipping tectonic contacts over the Bowmore and Colonsay Groups, and the West Islay Gneiss. The major difference in the regional tectonic settings of the Dalradian nappe pile in the South West Highlands, and that in the Central Highlands is therefore the composition and affinity of deeper level crust over which post-Grampian Division rocks are emplaced. However, further differences in lithology within the Dalradian sequences in both regions are apparent, with substantially more mafic rocks in the South West Highlands than in the rest of the Dalradian. Both these contrasts, in the composition of the crust over-ridden by post-Grampian Division rocks, and in the Dalradian lithologies themselves, have had a demonstrable additive effect on the contrasting metamorphic evolution of the Dalradian.

In both regions, the major structures have similar geometries, with flat-lying south-east verging structures (the Tay Nappe) being separated by steeply inclined to vertical structures from shallow-dipping north-west verging structures. Of these three groups of structures, only one, the Tay Nappe, can be traced unequivocally across the Cruachan Lineament. However, all the structures in both regions have enough in common to suggest that they all formed initially during the same deformational episode; the contrasts in the structures between the two regions therefore result from the later modifications which occurred subsequent to the primary, D1-D2, deformation. In the Central Highlands, these modifications were more pervasive than in the South West Highlands; this study has indicated that the reason for this difference is that the South West Highlands crust reached close to its highest temperatures at the time of the nucleation and propagation of the Tay Nappe and that these temperatures were lower than the highest temperatures
attained elsewhere in the Dalradian. Though cooling rates were slow throughout the South West Highlands after the D1-D2 deformation, only the deeper structural levels are likely to have undergone significant heating after the primary metamorphism, and these areas have the most complex metamorphic and deformational histories.

Thus, the Scottish Dalradian is characterised by an early episode of recumbent folding, and nappe formation, which has affected the whole region, and which is associated with compression. Therefore, the significance of this study for the orogenic evolution of the Dalradian is that more of the early deformational history is preserved in the South West Highlands than anywhere else in the sequence.

At present, there is little constraint on the plate tectonic events that lead to the Dalradian primary deformation and resulting metamorphism. However, the possible solutions of the thermal models in chapter 7 indicate that the emplacement of the West Islay Gneiss and overlying sediment in the South West Highlands took place at about the same time as the D1-D2 deformation. If this interpretation of the thermal models is a reflection of geological reality, a plate tectonic explanation for the nucleation and growth of the Tay Nappe is apparent, which is wholly consistent with the new time constraints available on Dalradian Metamorphism described in this thesis. Whether similar processes occurred in the Central Highlands, but with the Grampian and Central Highland Divisions being the equivalent to the wedge of Islay Gneiss and Bowmore and Colonsay Sandstones, is unconstrained at present, but remains a possibility.

The possibility that West Islay and Colonsay were part of a suspect terrain has already been addressed in chapter 7. Essentially, the West Islay-Colonsay region has a number of characteristics in its geological history which distinguish it from the rest of the Scottish Caledonides, the most important of which are the presence of pre-D1-D2 deformation in rocks subsequently involved in regional metamorphism and deformation also affecting Dalradian rocks, and the presence of an isotopically distinct gneissic basement (Marcantonio et al. 1988). The timing of the pre-D1-D2 deformation is constrained to have been prior to 600 Ma ago by unpublished Ar-Ar age data on amphiboles, and the best-fit solutions to the South West Highlands metamorphism for the thermal models in chapter 7 result if the gneiss wedge, emplaced at some stage in the Dalradian metamorphism, was cool on emplacement. Thus, though some tectono-metamorphic activity took place in
the Islay-Colonsay region prior to Dalradian metamorphism, the best-fit results of the models are derived if this metamorphism occurred early enough for the rocks affected to have cooled down prior to their emplacement beneath the Dalradian.

The Central Highland Division underwent pre-D$_1$-D$_2$ deformation at about 750 Ma, during the Morarian "orogeny". If the Central Highland and Grampian Divisions, and the West Islay Gneiss and Colonsay and Bowmore Sandstones are to be considered equivalent crustal segments in the South West and Central Highlands, respectively, the pre-D$_1$-D$_2$ deformation in the Colonsay Group would have to be a Morarian event, and would therefore invite correlation of the Colonsay Group with the Central Highland Division, and hence the Bowmore Group with the Grampian Division. A similar suggestion was made by Roberts (1974) on sedimentological grounds based on the Grampian Division being part of the Moine supergroup. The scenario just outlined would mean in turn that the West Islay-Colonsay region is not as distinctive in its geological history as Bentley et al. (1988) would suggest.

Another possibility for the pre-D$_1$-D$_2$ deformation on Islay and Colonsay is that it occurred as a result of the crustal thickening that is required by the thermal models to have occurred prior to the D$_1$-D$_2$ deformation. The thermal models suggest that this thickening would have occurred at between 540 and 560 Ma ago, but so far, no trace of such a deformation has been found.

The discussion so far in this section has been mainly conjecture, but it is hoped that it gives some idea of the problems and questions that have arisen from the results of this study.

As far as the orogenic history of the Dalradian is concerned, this study has shown that the Tay Nappe formed and nucleated at depth in an already-thickened crust, with depths great enough to give temperatures high enough to result in the growth of biotite and garnet grade assemblages. This conclusion stands no matter how well constrained the anomalously high pressures of metamorphism are that have been made in chapter 5. It also follows from the ca. 520 Ma ages derived by Dempster (1985) for Dalradian D$_1$ micas from the Highland Border. Hence the Tay Nappe could not have formed during the initial thickening phase of the Dalradian metamorphism; this phase must have taken place at some time earlier than the emplacement of the Tay Nappe. This is the major firm implication of this study for the tectonothermal history of the Dalradian. The study has also resulted
in the postulation of a mechanism for the formation and growth of what is one of the most important structural entities in the Scottish Caledonides, namely the emplacement of rock, either the Islay Gneiss in the South West Highlands, or, possibly, the Central Highland and Grampian Divisions in the Central and Southern Highlands, from the north-west beneath the already thickened Dalradian pile, but this mechanism is still hypothetical, for reasons discussed above.

The study also shows that models for the growth of the Tay Nappe, which imply that it formed as a shallow level feature (e.g. Harris et al. 1976, Roberts 1974, Shackleton 1979, Treagus 1987, Anderton 1988), its recumbency resulting from gravitational collapse, are untenable, because both the geochronological results and the presence of biotite and garnet grade mineralogy, show that the Crust undergoing deformation to form the Tay Nappe was at deep levels in the crust at the time of its formation. Estimates for this depth from pressure estimates are of the order of 32 to 40 km. Thus the most likely mechanism for the growth and propagation of the Tay Nappe is a rolling-hinge model, the fold remaining inclined to recumbent throughout its formation. The geometries of isograds which formed during the Tay Nappe emplacement are most consistent with the recumbent attitude of this fold at this time, based on simple thermal constraints.

This study has also illustrated how more than 100 Ma time-scales are needed for Dalradian metamorphism to occur, since the complete burial/heating-cooling/uplift cycle is constrained to have taken at least this length of time from the results of this study and of similar studies of other regions in the Scottish Dalradian. Thus, models suggesting for example that ophiolite nappes were emplaced at ca. 500-520 Ma ago (Dewey and Shackleton 1984), or that the Iapetus ocean opened at the time of the emplacement of the Tayvallich Volcanics (Anderton 1985, 1988), are unlikely to be consistent with the time-scales needed for Dalradian regional metamorphism. Essentially, such models do not allow enough time for the Dalradian metamorphism as observed in this, and other recent studies (Dempster 1985, Harte 1988), to occur.

8.1.2 Isograds and Metamorphic Zonation:

The probable surface exposure and possible three-dimensional geometry of isograd surfaces in the South West Highlands was discussed in sections 3.5 and
3.6. it being concluded that deeper levels in the crust reached higher metamorphic grades. This simple conclusion negates the possibility of inverted metamorphic zonation, and several arguments were presented to suggest that studies which inferred the presence of such zones were flawed. This was because the isograds drawn in such studies almost certainly represent the boundaries between zones dominated by contrasting bulk rock compositions. The result of these contrasts was the growth of differing assemblages, reduced lithologies with Barrovian almandine-grossular garnet-bearing assemblages being formed at higher levels, and oxidised lithologies with biotite- and almandine-grossular garnet-absent assemblages at deeper structural levels. The higher f-O2 rocks were also pervasively overprinted by secondary, albite porphyroblastic assemblages (see also section 4.2) adding to the apparent differences between the deeper level, and the shallower level lithologies.

The presence of inverted metamorphic zonation could not be disproved with the evidence presented in sections 3.5 and 3.6, but it was pointed out that for inverted zones to be preserved, cooling and uplift rates after D1-D2 deformation would need to be rapid. All the evidence presented in this thesis shows that this was manifestly not the case, but that cooling rates were uniformly slow, with little variation over time and across-strike. The steady uplift throughout the metamorphic evolution of the South West Highlands has therefore resulted in a simple isograd geometry for the region, the only complication being in Northern Kintyre, where the secondary overprinting assemblages are concentrated. The Balquidder area, where inverted metamorphic zonation was inferred, has an identical metamorphic and assemblage growth history to the South West Highlands, so it is reasonable to infer that the uplift and cooling history of that region was also similar, but complicated by the near presence of the presumably warmer crust to the north-east of the Cruachan Lineament.

However, the Central Highlands shows much evidence for complex metamorphic zonation, with abrupt metamorphic field gradients, particularly to the north-east of the Scottish Dalradian outcrop where the Buchan zones and the Barrovian type area meet across the Portsoy-Duchray Hill Lineament, but are also seen in other areas in this region, especially the high-pressure overprinting episodes associated with the Tarfside Culmination (Harte and Dempster 1986), and the narrowing of isograds across the Cruachan Lineament (eg Fettes 1979, see also the figure in Harte 1988). These complications are clearly manifestations both
of the short length-scale variations in the crustal structure of the Central and Eastern Highlands inferred by Fettes et al. (1986), and of the complex and protracted uplift histories in this region. These two manifestations probably have the same root causes: the differences in the pre-metamorphic histories of the region. As a result, the structure and geometry of metamorphic zones in the Central and Eastern Highlands will inevitably be more complex than in the South West Highlands.

The Dalradian therefore shows much variability in its metamorphic history, with almost the entire spectrum of metamorphic P-T conditions in Miyashiro's facies series being exhibited. These variations are closely linked to the crustal structure and composition and are the main reason why this study has implications for the study of regional metamorphic processes as a whole. These implications will be discussed in the next section.

8.2 Implications for Controls of Regional Metamorphic Processes:

The main conclusion of this study is that high-pressure low-temperature assemblages can be preserved as the first-formed, and dominant, assemblages grown over regional scales in an area which has undergone slow cooling and uplift. This study has shown how the localised variation in crustal structure and lithological composition results in localised variations in the tectono-metamorphic evolution of the region. Thus, the major control on metamorphism was the rate of crustal heat production. Since this was low in the South West Highlands in comparison to other regions of thickened continental crust throughout the world, the highest temperatures attained in the thickened crust were also low. In combination with a crustal composition that is resistant to deformation due to the high shear strength of the large proportion of mafic lithologies present, these relatively low peak temperatures have also inhibited deformation subsequent to the primary nappe emplacement episode and have therefore aided the preservation of the early-formed assemblages.

Thus, as already stated in the previous section, the extent of metamorphism and deformation in the Dalradian region was controlled by the highest temperatures attained, this in turn being controlled by the heat production rates in the metamorphosed crust. As a result, the area with a relatively simple isograd
structure, the South West Highlands, also has a relatively simple deformational history, while the region with complex metamorphic structures also has a complex deformational history. Thus, throughout the Dalradian, metamorphism is inextricably linked with deformation.

Similar relationships are also seen in younger mountain belts in which short time-scale processes are more likely to be preserved. The best example of these relationships elsewhere in the world is in the Himalaya where the well-known inverted isograd sequence associated with the Main Central Thrust is exposed (Le Fort 1975). In addition, cordilleran metamorphic core complexes (e.g., Coney 1980) have steep metamorphic gradients associated with them and are usually Tertiary in age. Both these examples are of regional metamorphic assemblages intimately associated with deformation in space and time which formed over short time-scales. Metamorphic structures in the Dalradian with short length-scales are also present, as is evidence for short time-scale metamorphic processes. The one region in the Scottish Dalradian where such features are conspicuous by their absence is the South West Highlands.

Thus, while deformation in the South West may have been transient when it occurred, it was sufficiently simple that the isograds that resulted from the accompanying metamorphism have a simple geometry and steep metamorphic gradients are absent. In contrast, the deformational history in the Central, Southern and Eastern Highlands was complex, such that metamorphism occurred at different times in different parts of a dynamically evolving mountain belt, resulting in the preservation of a wide range of mineral assemblages and metamorphic facies.

8.3 Outstanding Problems Arising From This Study:

It is against the nature of scientific enquiry to suggest that a comprehensive study can be carried out without raising new, unanswered questions. Some of these questions arising from this study and concerning the pre-$D_1$-$D_2$ history of the region have already been discussed, and these and other questions will be summarised below.
8.3.1 The Caledonian Orogeny; Outstanding Problems:

For the purposes of this discussion, a rather all-embracing definition of the Caledonian orogeny, as it affects the Scottish Highlands north of the Highland Border Fault, will be adopted as being those tectono-metamorphic events which affected all the Moine and Dalradian rocks, as well as those rocks of uncertain affinities along the boundaries of the two supergroups just mentioned. Thus, this blanket definition includes the Grenvillian and Morarian "events", as well as the Caledonide/Grampide (s.s.) orogeny itself, and includes the West Islay-Colonsay Terrain as well as the Highland Border Series ophiolites.

A major outstanding problem is the status of the West Islay-Colonsay region as a suspect terrain. Though much geochemical, structural and stratigraphic evidence points to this region having its own, discrete, geological history, prior to its emplacement beneath the Dalradian, the major unsolved problem which would help shed light onto some of the speculations in section 8.1 is the age of the pre-D₁-D₂ deformation in Colonsay. I have already suggested that the available evidence cannot rule out a Morarian age for this deformation. The conclusions of this thesis would be favoured by, but do not require, such an age. The other alternative, also already suggested, but inconsistent with the relatively scanty available evidence is that this deformation represents the pre-D₁-D₂ crustal thickening event required by the syn-D₁D₂ primary metamorphism in the South West Highlands.

The major area for potential further study is therefore a comprehensive geochronological program on the phengite fabrics formed as a result of this deformation. The Rb-Sr method should, at least in theory, give some constraint as to the timing of this event because the closure temperature of this system is relatively high, but the complexities associated with the dating of phengites with the Rb-Sr method, notably the resetting of phengite ages, will make such a program less than straight-forward. These complexities are discussed next.

8.3.2 Petrology and Geochronology in Low- to Medium-Grade Pelites; Outstanding Problems:
8.3.2.1 Thermodynamics of Pelitic Assemblages:

The detailed descriptions of mineral chemistries in the primary and secondary pelitic assemblages have shown how these are dominated by the TS exchange, and how the resulting mineral chemistries are ultimately affected by rock bulk-composition, as well as the P-T conditions of metamorphism. The P-T-XTS sections of section 5.1 are an elegant way of illustrating some of these relationships (see also Pattison 1987), but they are only semi-quantitative at best. An internally consistent set of thermodynamic calibrations of the reactions and nets derived would be of great value because the assemblages to which they are applicable are very common, but are difficult to characterise with respect to the P-T conditions of metamorphism. There have already been attempts to calibrate some of these reactions; most of these calibrations have been applied in this thesis in chapter 5. These calibrations, especially the comprehensive series of experiments by Massonne and Schreyer (1987) would form a suitable basis for this work.

8.3.2.2 Reactions and Assemblages in Pelites:

The South West Highlands has a wide variety of bulk rock compositions that have been metamorphosed under similar P-T conditions, but have produced a range in mineral assemblages and compositions as a result of the bulk chemical differences inferred. Thus, assemblages produced in oxidised bulk-rocks are chloritic with spessartine-rich garnet and are usually biotite-free, while other high Al/Si ratio bulk rock compositions have preferentially stabilised biotite instead of chlorite, even in secondary assemblages and in Mg-rich compositions.

A start has been made in this study concerning some of these assemblages, but more work could easily be done, especially on the oxidised schist (high-modal-chlorite pelites) horizons. Such work might be concerned with the role and detection of high f-O₂ conditions at low to medium grades, especially because f-O₂ is difficult to characterise in rocks of this grade. Such work might also study the processes which result in the growth of porphyroblastic albite, which is common in high-pressure, low- to medium-temperature metamorphic belts throughout the world including, of course, the South West Highlands.
8.3.2.3 Rb-Sr Systems in Phengites:

It has been shown that kinetics of reactions involving phengite are sluggish, with respect to major elements, even when some deformation is present. However, some of the Rb-Sr geochronological results are consistent, both with very slow cooling rates, and with rapid resetting of the Rb-Sr system in phengites by deformation, even when no penetrative fabric is formed. The most pressing problem, which may yet prove intractable, is the absence of diffusion data for Sr in phengite. Though the South West Highlands with its well-characterised temperatures of metamorphism and rates of cooling would make a well-suited natural laboratory for this problem, unravelling the effects of closure and resetting from a comprehensive series of mineral ages may prove difficult. However, splitting of mineral separates into chemically distinct fractions by magnetic separation (see appendix 1), accompanied by analyses of these fractions (XRF? Probing of grain mounts?) and by measurement of zoning of Sr in phengite with the ion probe, may yet prove fruitful. This problem may need to be resolved because the Rb-Sr dating of well-characterised phengite fabrics should be a highly effective way of timing deformational events in a polymetamorphic terrain.

The results of this study have shown that The South West Highlands cooled very slowly in comparison with other regional metamorphic belts, the rates of cooling calculated from differing constraints being in close agreement with one another at ca. 1 to 4 °C, these constraints being the differences between cooling ages from samples with are likely not to have been affected by post-primary metamorphic re-equilibration, the estimates of cooling rates from reset garnet zoning, and the estimates of closure temperature variation in phengites that have been made. These cooling rates have been remarkably constant throughout the uplift history of the South West Highlands, especially when compared with Perthshire and Angus (Dempster 1985).

As a result, the South West Highlands should make a particularly effective natural laboratory for study of the behaviour of elemental and isotopic systems in rocks. The temperature-time history of the region is well characterised, as are the chemical trends in the minerals concerned with time.
8.3.3 Regional Metamorphic Processes; Outstanding Problems:

Many of the speculations made in this and other chapters concerning the controls on the geometry of isograds, and on the degree and extent of deformation, depend on inferences drawn from the application of models, not to the South West Highlands, but to other areas and problems. Thus, I have suggested that deformation in the South West Highlands is controlled by the competence of the lithologies, this competence being controlled in turn by lithology, mineralogy and temperature. Justification for this suggestion is based on the results of Kuznir and Park's (1986) models of sedimentary basin evolution where a similar range in lithologies to that in the South West Highlands is present. I have also suggested that inverted isotherms will only result if strain rates are high, without attempting to quantify what strain rates are needed. Other potential problems that have been speculated upon, but which remain unmodelled, are the effect of heat advection by the emplacement of the Tay Nappe on the subsequent cooling history of the South West Highlands and the possibility of significant heat transfer in more than one dimension in the thickened Dalradian crust at the time of the primary metamorphism (the suggestion being that both these possibilities will enhance cooling rates in the higher grade regions of the South West Highlands after the primary metamorphism).

The first hypothesis, that of competence control on deformation, would be testable by strain rate calculations under a given stress. Since this calculation is relatively straightforward, its results are relatively predictable; this hypothesis can therefore be accepted relatively confidently. However, if carried out, strain rate calculations would also allow the suggestions concerning heat advection by the Tay Nappe to be tested. As described in chapter 3, high enough strain rates may result in the overturning of isotherms and resultant rapid, but transient, temperature changes in the crust volumes concerned. Calculation of the Peclet number for such a scenario for different strain rates would be relatively straightforward, since length-scales (the wavelength and amplitude of the Tay Nappe) are well known.

Doubtless there are other questions to be answered arising from this thesis and its contents, but hopefully this section will give some indication as to what directions future research on the South West Highlands relating directly to this study might take.
8.4 Concluding Statements:

This thesis has sought to illustrate the controls on regional metamorphism in the South West Highlands. These have been shown to be the composition and structure of the crust undergoing orogeny, which in turn are functions of the pre-metamorphic histories of the regions. Thus, Dalradian metamorphism can be shown to be explicable in terms of the dynamic regional stratigraphy, rather than as a mysterious event with complications to be explained in an ad hoc way. The complications and local variations in the metamorphic history of the Dalradian are related intimately to local variations in lithological compositions and crustal structures, which in turn are related to variations in the pre-metamorphic and depositional histories of the region. Thus, the geological history of the region had no vestige of a beginning.

"I have long wished to finish this task....."

The Orestria,

"This is the best of me...."

Sir Edward Elgar, dedication on the autograph score of "The Dream of Gerontius"
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Appendix I; Isotopic Techniques:

Sample Preparation:

**Mineral Separation**

The geochronology described in chapter 6 was carried out on mineral separates and whole-rock powders from each sample. 1-5 kg-sized masses of sample were first crushed in a steel jaw crusher, to a size of about 0.5 to 1.0 cm and weathered fragments hand-picked out. The sample was also roughly sieved through 0.5 cm and 200 μm mesh-sized sieves after each pass through the jaw crusher both to minimise crushing and risk of Ar loss, and to remove weathered material which tended to crush down preferentially. The 200 μm to 0.5 cm size fraction was retained, and the >0.5 cm fraction was jaw-crushed again.

The whole-rock powders were produced by grinding hand-picked for freshness ≈1 cm-sized chips of the jaw-crushed rock in a large tungsten carbide swing mill for about 1 minute. The rest of the jaw-crushed sample was also crushed in the same swing mill, but for less than 10 seconds, so that much of the material resulting was between 50 and 200 μm in size. This was then washed in water until the dust in the sample was removed, then washed in acetone, then dried in an oven at 70 °C. The drying usually took overnight. During the course of the separation work, it was found that crushing 0.2-0.5 cm-sized fragments in the large swing-mill under water for 5 minutes, then sieving and washing, was particularly effective at concentrationing micas and chlorite in the sample. This was due to the sheet silicates dis-agregating preferentially along cleavage planes, while the quartz and feldspar in the rock crushed down to a powder. This method meant that far smaller samples could be used to derive enough mica concentrate to carry out mineral separation.

The dried sands were then sieved according to the grain-size of the specimen, the size fractions resulting usually being between 100 and 200 μm, but sometimes smaller from the lower grade assemblages. Separation of <50 μm grain sizes necessary for some of the lower grade assemblages proved to be intractable.
Mineral separation was carried out using mainly the Franz isodynamic magnetic separator for micas, but also using iodo-methane for amphibole separation, diluted to specific gravities appropriate for each sample with acetone. The diluted iodomethane could be recovered by boiling under vacuum. Although a given mineral from different assemblages was concentrated by a given Franz setting, or specific gravity of iodomethane, the correct settings could be found only by trial and error, though the variation between assemblages was not usually large. Mineral separating is therefore a challenging, sometimes tedious, and sometimes exasperating, pass-time which requires tenacity and application.

Ball-park estimates of magnetic susceptibilities and specific gravities were made from the tables and diagrams in the C.R.C ("rubber bible") handbook, and from "Geological Laboratory Techniques" (Allman and Lawrence 1972). Usually, the sieving avoided intergrowths of different phases, but where present, effective disaggregation by grinding under alcohol with an agate pestle and mortar resulted.

Sometimes, prior to use of the Franz, micas were concentrated by the shaking table. Because of their shape and aspect ratio, micas tended to remain on the table surface, while quartz, feldspar and amphiboles tended to roll down the table. Again, trial and error with shaking intensities and surfaces was required. Grain mounts of the concentrates were examined frequently, and the samples were assessed as being pure when no impurities were visible on examination of ca. 50 to 100 grains. Thus, impurities made up less than 1-2 % of the sample.

Approximate Franz settings for most of the specimens worked on were:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Side Slope</th>
<th>Forward Slope</th>
<th>Current Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phengite from quartz and feldspar</td>
<td>15°</td>
<td>20-40°</td>
<td>1.125 amps</td>
</tr>
<tr>
<td>Biotite chlorite and amphibole</td>
<td>15°</td>
<td>20-40°</td>
<td>0.4-0.5 amps</td>
</tr>
<tr>
<td>Biotite from chlorite</td>
<td>10°</td>
<td>20-40°</td>
<td>0.3-0.4 amps</td>
</tr>
</tbody>
</table>

Thus, biotite, chlorite and amphibole (where present) were concentrated as a
group from another group of less magnetic phases. The magnetic group was then split into individual phases by more careful use of the Franz, and, where appropriate, iodomethane. The less magnetic group of phases includes phengite, which was separated from the other phases by the higher current settings on the Franz. The effect was therefore to tend to concentrate the more magnetic, hence more celadonitic, phengite, because less magnetic phengite had more quartz and feldspar impurities associated with it. This is the reason why it is possible that older phengites may have been preferentially sampled during mineral separation in some of the garnet zone samples (section 6.5). The method used for assessing sample purity would be effective for micas, because intergrowths etc. are relatively easy to recognise, the grains being relatively transparent and thin. However, fine-scale intergrowths in amphiboles would be difficult to recognise optically because of the probable smaller size of these, and because of the larger grain-size of the amphiboles making it harder to see through them.

Chemical Preparation of Samples:

Rb-Sr Methods:

All laboratory ware was subject to multi-stage ultra-cleaning before use, by successive overnight soaking in HNO₃ and HCL and rinsing in 2X distilled water, then drying. All chemical preparation was done in clean labs with positive air pressures. Samples were weighed into teflon beakers, along with standard solutions, or spikes, of known isotopic concentration. ⁸⁷Rb (99.2%, Harwell) and ⁸⁴Sr (99.78%, N.B.S.) spikes were used. Problems with static electricity were encountered, particularly with biotites, but wrapping the teflon beakers with aluminium foil, and using an anti-static gun reduced these problems dramatically.

Acid Attack and Dissolution:

Samples were attacked initially with a mixture of 1 part 2X distilled 16 N HNO₃ and 8 parts HF, and the samples heated to 150°C for at least 8 hours. Despite the coarse grain-size of some of the samples, no problems with incomplete dissolution were encountered. The samples were then heated to dryness at 200°C, usually taking 2 to 5 hours. Then 2X distilled water was added, followed by a similar amount of 2X distilled HNO₃, and the samples were, again,
left overnight at 150°C. After drying, 6N HCL was added to the sample, and again left overnight at 150°C. Then, on drying, 2X distilled, 16N HNO₃ was added, and the samples dried immediately. Finally, about 2.5 ml 2.5N HCl were added to the samples which were then sealed.

Ion Exchange:

Ion exchange was carried out using 2.5N HCl as an exchange medium, using Bio-Rad AG50 W-X8 200-400 mesh resins which are calibrated frequently with pure Sr solutions. The samples, now in solution in 2.5N HCl were centrifuged for 5 minutes, and 2 ml of each solution was added to the cleaned columns. Then 2.5N HCl was passed through each column and Rb and Sr solution collected, the amounts of acid necessary being decided by previous calibration of the columns. On collection of Rb and Sr, each sample was heated to dryness, then the Sr samples were treated with 1 drop of 2X distilled HNO₃, and both sets of samples were sealed.

K-Ar Methods:

K analyses were carried out at Edinburgh. Samples were weighed into platinum crucibles, and attacked with a mixture of HNO₃, H₂SO₄, and HF acids. The solutions were heated at about 150°C for several hours, then were heated at 200 °C to dryness, until no more acid fumes were given off by the samples. The samples were then diluted to 250 ml with deionised water. The crucibles were filled and emptied several times into the sample flask to ensure complete transfer of the solution. Glass vessels were avoided as much as possible, only being used for measuring, and not for storage. This is because glass has some K which can leach into solution.

Ar analyses were carried out by total fusion of samples weighed into copper capsules. No chemical preparation and dissolution was necessary.

Analytical Methods:

Rb-Sr Methods:

Both Rb and Sr were analysed by solid-source mass-spectrometry. Rb was
loaded in distilled water onto side filaments of three-filament outgassed tantalum beads, while Sr was loaded in phosphoric and hydorchloric acids onto single filament outgassed tantalum beads.

The samples were then ran on a VG micromass MM30 mass-spectrometer with automated data collection and peak switching, but with manual beam finding and focussing. Some of the samples were ran on a fully-automated VG IG54E mass-spectrometer. Accelerating potentials for both Rb and Sr were about 8 kv, and analyses were carried out under high vacuum of less than 10⁻⁷ torr. Prior to running, Sr samples were pre-heated at 1.9 amps for about 30 sec, and the centre filaments on the Rb beads were pre-heated for about 1 minute. Problems were sometimes encountered with maintaining the high vacuum when running Rb, since the loaded salt was deliquescent. Sometimes, drying prior to loading of the sample into the machine was necessary.

Rb was run on a centre filament intensity of about 2.5 amps and a side filament intensity of about 1 amp. The 85, 87 and peaks were scanned in sets of ten scans. Precision to 1 E-04 was usually gained within 10 sets, so that a Rb analysis took up to half an hour. Each peak was scanned for 1 second. Sr was run on a current intensity of about 2.3 to 2.5 amps. The 84, 86, 87, and 88 peaks were scanned for 1 second each and backgrounds were taken on 90.5. A set consisted of 15 scans, and precision (1 σ) of 5E-05 was achieved in between 30 and 50 scans, depending on the possible running intensities. These were relatively low, especially for biotites, due to the low Sr abundances in the samples.

Reproducibilities of ⁸⁷Sr/⁸⁶Sr from duplicate samples were usually better than 1E-04, which translated to errors on ages of usually less than 5 Ma. Thus, sample heterogeneity gave rise to errors similar to the statistical errors associated with the analytical methods. Rb and Sr abundances and isotope ratios were taken from Steiger and Jager (1976), and calculated using software written and developed by J. Hutchinson.

During the ca. three-year period in which analyses were carried out, analyses of NBS 607 produced ⁸⁷Sr/⁸⁶Sr ratios of 0.71028±05.

**K-Ar Methods:**

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K analyses for micas were carried out on a Corning-EEL flame photometer using an air-natural gas flame. This flame is relatively cool, so that interference from other elements is kept to a minimum. Sample solution K concentrations were found by bracketing between standard solutions with differences in concentrations of 1 ppm, where the solution concentration was about 10 - 20 ppm. The relationship between the reading on the photometer and solution concentration was assumed to be linear over the concentration interval. Analyses of NBS standard biotites resulted in K$_2$O abundances within 0.5% of the standard value, and reproducibility errors of less than 1 % also resulted from separate measurements of a given solution. Duplicate analyses on different aliquots of the same sample were also reproducible to ca. 1 %.

Amphiboles were analysed on a Varian flame atomic-absorption spectrometer using a propane flame. The methods of analysis are the same as those for K in micas, but reproducibilities were not so low, due to the lower K abundances. Swamping solutions from amphiboles with Na, and Rb did not affect the resultant K values significantly. Some of the solutions were also analysed by standard addition, which tended to give lower K abundances from a given solution than the standard bracketting method normally used. Reproducibility within a sample solution was usually within 2 %, but reproducibility between sample aliquots was sometimes as poor as 5 %. However, none of the reproducibility levels were large enough to explain the apparently young ages in most of the samples analysed.

Ar was analysed on a A.E.I 10 gas source mass-spectrometer, with manual scanning between 36, 38 and 40 Ar peaks whose heights were measured from chart recorder plots. Prior to each analysis, the charcoal getter and zeolite trap were outgassed, while prior to each batch of ten samples, the molybdenum furnace was outgassed. New furnaces are made up for each batch of ten samples. For each analysis, a known volume of spike $^{38}$Ar was let into the Ar extraction line. Ar being extracted from the sample by fusion in the molybdenum furnace heated in a water jacket by an induction coil. The sample and spike were cleaned in the heated zeolite, and in the two activated charcoal fingers, into which the sample was trapped by cooling with liquid nitrogen. Usually three complete scans between 40 and 36 and back to 40 were taken, the recorder being held on each peak twice, for up to 5 seconds, along with three automated scans across the 36

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peak to account for the "shoulder" effect of the much larger 38 peak. Between each peak measurement, background levels were taken, also for about 5 seconds each. Reproducibility errors for Ar ratios were less than 1 E-04. Usually, it was possible to run up to three samples for Ar in a long day.
Table of isotopic data:

Rb-Sr isotopic data:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb ppm</th>
<th>Sr ppm</th>
<th>Rb/Sr wt. %</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Age (Ma) $(\pm 2\sigma)$</th>
</tr>
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<td>85-11</td>
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<tr>
<td>Wr</td>
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<td>47.09</td>
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<td>591(Wr1), 522(Wr2)</td>
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<td>0.431</td>
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<td>&lt; zero(Wr2)</td>
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<td>37.48</td>
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<td>Wr</td>
<td>58.32</td>
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<td>4.31E-02</td>
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<td>263.7</td>
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<td>111.1</td>
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<td>0.77039±7</td>
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<td>30.27</td>
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<td>2.594</td>
<td>0.75853±14</td>
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<td>Bi</td>
<td>297.9</td>
<td>7.126</td>
<td>47.65</td>
<td>151.9</td>
<td>1.8122±</td>
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<td>Mu</td>
<td>261.6</td>
<td>59.92</td>
<td>3.877</td>
<td>11.34</td>
<td>0.82660±7</td>
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00 437
### K-Ar Isotopic Data:

<table>
<thead>
<tr>
<th>Sample</th>
<th>K₂O wt.%</th>
<th>K wt.%</th>
<th>( ^{40} \text{Ar} ) μmol g⁻¹</th>
<th>( ^{40} \text{Ar} ) rad.%</th>
<th>Age (Ma ± 2σ)</th>
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<tbody>
<tr>
<td>70-41</td>
<td>8.195</td>
<td>6.803</td>
<td>0.055</td>
<td>98.29</td>
<td>414.6 ± 9</td>
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<tr>
<td>85-25</td>
<td>9.341</td>
<td>7.759</td>
<td>0.073</td>
<td>98.01</td>
<td>472 ± 9</td>
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<tr>
<td>84-20</td>
<td>8.732</td>
<td>7.249</td>
<td>0.065</td>
<td>97.21</td>
<td>452 ± 9</td>
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<tr>
<td>86-6</td>
<td>9.483</td>
<td>7.872</td>
<td>0.075</td>
<td>91.35</td>
<td>443 ± 9</td>
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<tr>
<td>85-11</td>
<td>7.808</td>
<td>6.482</td>
<td>0.058</td>
<td>97.75</td>
<td>444 ± 9</td>
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<tr>
<td>86-2</td>
<td>5.902</td>
<td>4.900</td>
<td>0.049</td>
<td>93.49</td>
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<tr>
<td>85-24</td>
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<td>0.079</td>
<td>94.86</td>
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<tr>
<td>84-21</td>
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<td>69-102</td>
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<td>85-04</td>
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<td>69-06</td>
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<td>85-08</td>
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<td>0.293</td>
<td>0.0034</td>
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<td>69-204</td>
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<td>86-3</td>
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<td>435±9</td>
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<td>69-179B</td>
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<td>71-42</td>
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<td>0.0049</td>
<td>88.38</td>
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Table of Assemblages for Which Data are Given:

The following assemblages were analysed for Rb-Sr geochronology. Some were also analysed by the K-Ar method.

Sample 85-11: Locality, North-Central Knapdale, garnet isograd: semi-pelite with a planar, uncrenulated fabric, weathered: qz + pheng + bi + chl + ab

Sample 84-21: Locality, South Bay: very micaceous pelite with a high mode of k-feldspar-rimmed albite porphyroblasts in a complex fabric, primary garnet and biotite preserved in strain shadows, quartz-rich layers and as inclusions in albite porphyroblasts: pheng + chl + ab + bi + qz + gt + sph + rut

Sample 84-3: Locality, South Knapdale: biotite-bearing quartzite with a mildly crumpled fabric, no porphyroblastic albite and relatively little chlorite: qz + pheng + bi + chl + ab

Sample 84-8: Locality, East Loch Tarbert: green-biotite-bearing chlorite-absent semi-pelite with a highly crenulated fabric and albite porphyroblasts: qz + pheng + bi + ab

Sample 84-20: Locality, South Bay: Quartzitic semi-pelite with fresh garnet and biotite, and a weakly crumpled schistosity. No porphyroblastic albite: qz + pheng + bi + chl + gt + ab

Sample 85-24: Locality, Central-South Knapdale: quartzitic semi-pelite with a planar, uncrenulated fabric, no porphyroblastic albite: qz + pheng + bi + chl + ab

Sample 85-23: Locality, South Knapdale: quartzitic semi-pelite with a planar, uncrenulated fabric similar to 85-24, but distinctly more quartz-rich and more massive: qz + phen + bi + chl + ab

Sample 84-46: Locality, Carsaig, Tayvallich Peninsula: Very gritty psammite with fine grained, almost sericitic phengite intergrown with chlorite, much clastic feldspar: qz + fdsp + pheng + chl + tourm
Sample 85-25: Locality, North-Central Knapdale: A biotite-free semi-pelite with a planar fabric: qz + pheng + chl + ab

Sample 85-14: Locality, Ardrishaig: Highly micaceous and carbonaceous phyllite with a strongly micro-folded fabric: pheng + chl + carbonate + qz

Sample RG3: Locality, Loch Cailosport: similar to 85-14

Sample JM2: Locality, Tayvallich Peninsula: carbonate with a planar fabric: carbonate + pheng + chl + qz

Sample 86-22: Locality, S.W. Jura: Micaceous semi-pelite but with little or no crenulation: phen + chl + qz + ores

Sample 87-11: Locality, Northern Kintyre: biotite-free semi-pelite with a planar, but re-activated, fabric overgrown by small albite porphyroblasts, small pristine spessartine-rich garnets are common: qz + pheng + chl + ab + gt

Sample 87-10: Locality, Northern Kintyre: biotite-bearing semi-pelite with a planar fabric, and no porphyroblastic albite: qz + pheng + bi + chl + ab

Sample 86-8: Locality, Kennacraig Pier, West Loch Tarbert: almandine-grossular garnet and biotite-bearing semi-pelite with a slightly crenulated fabric and coarse, clastic feldspar: qz + pheng + chl + bi + gt

Sample 87-18: Locality, Northern Kintyre: similar to 87-10

Sample 87-20: Locality, Northern Kintyre: highly micaceous and chloritic semi-pelite with a planar but re-activated fabric, and albite porphyroblasts growing within: pheng + chl + qz + ab

Sample 85-10: Locality, North-Central Knapdale, garnet isograd: chlorite-absent, biotite-bearing semi-pelite with an entirely planar and uncrenulated fabric: qz + pheng + bi + ab

Sample 86-4: Locality, Northern Kintyre: semi-pelite with a strongly crenulated fabric, no albite porphyroblasts or biotite: qz + pheng + chl
Sample 84-26: Locality, South Knapdale: Biotite-bearing, chlorite-absent quartzitic semi-pelite with mild crumpling of the fabric: qz + pheng + bi + ab

Sample 86-5: Locality, Northern Kintyre: As 86-4

Sample 86-10: Locality, North-Central Knapdale: semi-pelite with an entirely uncrenulated planar fabric, relatively high mode of sheet silicates: qz + chl + bi + ab

Sample 69-217BH: Locality, Tayvallich Peninsula: carbonate with a well-defined planar fabric and little or no chlorite: carbonate + pheng + qz ± chl

The following samples were used for K-Ar geochronology only.

Sample 86-6: Locality, West Loch Tarbert: strongly crenulated, chlorite-rich, biotite-free semi-pelite: qz + chl + pheng

Sample 86-2: Locality, Tayvallich Peninsula: gritty psammite with a strong planar shear fabric, very high mode of ore phases and green biotite: qz + fdsp + pheng + bi + chl + ores

Sample 86-3: Locality, Claonaig, Northern Kintyre: finer-grained semi-pelite with a strongly crenulated fabric: qz + chl + pheng + ab

Sample 84-9: Locality, East Loch Tarbert: green-biotite-bearing chlorite-free albite porphyroblastic semi-pelite with a strongly crenulated fabric: qz + pheng + bi + ab

Samples 69-204 and 85-04: Locality, Crinan: amphibolite with inter-grown hornblende and actinolite: hbl/act + ab + chl + qz

Sample 70-41: Locality, South Knapdale: Mg-rich amphibolite with high modal biotite: act + bi + ab + chl

The following samples are all hornblendic metabasic assemblages from Central and Southern Knapdale, with the assemblage hbl + ab + chl + sph + qz:

69-102, 70-48, 69-179B, 70-37, 70-148
Samples 69-06 and 85-08: Both these are actinolite-bearing assemblages from the biotite zone, 69-06 from Crinan, and 85-08 from Castle Sween: act + chl + ab + qz
Appendix II; Electron Probe Analyses; Data and Methods:

During the course of this study, many specimens were analysed by the electron probe and some of the resulting data is reproduced below. The data compilation is representative of the assemblages discussed in detail in this thesis. Some analyses were also performed by Dr. C.M. Graham; these are distinguished by the letters CG in the analysis numbers. All the mineral formulae and activities were calculated by the program METAMIN (Winterburn 1987) using the ideal mixing on sites formulations of Powell and Evans (1983).

The instrument used was the Edinburgh University Cambridge Instruments Microscan instrument. The operating voltage was 20 kv, and the beam current was 30 mA. The sample penetration depth is about 4 μm for this beam, and the beam diameter is about 1-2 μm. Natural and artificial standards for Si, Al, Fe, Mg, K, Na, Ca, Ti, Cr, and Mn were read prior to each probe session, and repeated when necessary. Corrections for dead-time, atomic number, atomic absorption and fluorescence were applied automatically with software developed at Edinburgh by P. Hill and D. Russell, using the methods of Sweatman and Long (1969). Further details are found in Winterburn (1987), Thirlwall (1979), and Russell (1985). Detection limits and errors are given by Winterburn (1987, p. 378), and are of the order of 0.1 wt%. Analyses were taken with the WDS system, with four peak counts and two background counts, each of ten seconds, for each element.
SiO₂: 48.27  MgO: 2.14  CaO: 0.02  Cr₂O₃: 0.00
Al₂O₃: 26.16  FeO: 5.45  Na₂O: 0.33  B₂O₃: 0.00
TiO₂: 0.37  MnO: 0.01  K₂O: 10.04  Total: 99.70

SiO₂: 48.65  MgO: 2.61  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 27.23  FeO: 5.13  Na₂O: 0.31  B₂O₃: 0.00
TiO₂: 0.38  MnO: 0.02  K₂O: 10.78  Total: 95.11

Si: 3.308  Mg: 0.228  Ca: 0.002  Cr: 0.000
Al: 2.205  Fe₂: 0.326  Na: 0.046  Ba: 0.000
Ti: 0.020  Mn: 0.001  K: 0.916  Sc: 0.000

Si: 3.316  Mg: 0.265  Ca: 0.000  Cr: 0.000
Al: 2.188  Fe₂: 0.292  Na: 0.041  Ba: 0.000
Ti: 0.019  Mn: 0.000  K: 0.937  Sc: 0.000

SiO₂: 47.18  MgO: 2.42  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 26.41  FeO: 6.17  Na₂O: 0.35  B₂O₃: 0.00
TiO₂: 0.42  MnO: 0.03  K₂O: 10.36  Total: 93.34

SiO₂: 48.90  MgO: 2.90  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 26.24  FeO: 5.19  Na₂O: 0.31  B₂O₃: 0.00
TiO₂: 0.31  MnO: 0.02  K₂O: 10.50  Total: 94.46

ROCK NO: 86-50  MUSCovITE  ANAL NO: 67  Mclide  3
ROCK NO: 87-22  MUSCovITE  ANAL NO: 78  Mclide  3
ROCK NO: 86-50  MUSCovITE  ANAL NO: 68  Mclide  4
ROCK NO: 87-22  MUSCovITE  ANAL NO: 74  Mclide  4
ROCK NO: 88-50  MUSCovITE  ANAL NO: 69  Mclide  5
ROCK NO: 87-22  MUSCovITE  ANAL NO: 80  Mclide  5
ROCK NO: 87-12  MUSCovITE  ANAL NO: 70  Mclide  1
ROCK NO: 87-22  MUSCovITE  ANAL NO: 81  Mclide  6
ROCK NO: 86-50  MUSCovITE  ANAL NO: 67  Mclide  3
ROCK NO: 87-22  MUSCovITE  ANAL NO: 78  Mclide  3
ROCK NO: 86-50  MUSCovITE  ANAL NO: 68  Mclide  4
ROCK NO: 87-22  MUSCovITE  ANAL NO: 74  Mclide  4
ROCK NO: 88-50  MUSCovITE  ANAL NO: 69  Mclide  5
ROCK NO: 87-22  MUSCovITE  ANAL NO: 80  Mclide  5
ROCK NO: 87-12  MUSCovITE  ANAL NO: 70  Mclide  1
ROCK NO: 87-22  MUSCovITE  ANAL NO: 81  Mclide  6
<table>
<thead>
<tr>
<th>ROCK NO.</th>
<th>NO.</th>
<th>MINERAL FORMULA</th>
<th>NO. OF OXYGENS</th>
<th>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</th>
<th>THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>86-50</td>
<td>65</td>
<td>SiO₂: 48.90 MgO: 2.24 CaO: 0.00 Cr₂O₃: 0.00</td>
<td>11.</td>
<td>Si: 3.348 Mg: 0.228 Ca: 0.000 Cr: 0.000 Al: 2.180 Fe₂: 0.294 Na: 0.049 Ba: 0.000 Ti: 0.013 Mn: 0.000 K: 0.921 Fc: 0.000</td>
<td>A(MUSC) = 0.4555675983 A(CELAD) = 0.1291699409 A(CELAD) = 0.0000000000</td>
</tr>
<tr>
<td>86-50</td>
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<td>SiO₂: 47.46 MgO: 2.16 CaO: 0.000 Cr₂O₃: 0.000 Al₂O₃: 26.38 Fe₂O₃: 5.23 Na₂O: 0.35 BaO: 0.000 TiO₂: 0.38 MnO: 0.005 K₂O: 10.59</td>
<td>11.</td>
<td>Si: 3.330 Mg: 0.225 Ca: 0.000 Cr: 0.000 Al: 2.180 Fe₂: 0.306 Na: 0.047 Ba: 0.000 Ti: 0.020 Mn:0.003 K: 0.444 Fc: 0.000</td>
<td>A(MUSC) = 0.4617755867 A(CELAD) = 0.1291444250 A(CELAD) = 0.0000000000</td>
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<tr>
<td>87-12</td>
<td>72</td>
<td>SiO₂: 48.29 MgO: 2.52 CaO: 0.13 Cr₂O₃: 0.000 Al₂O₃: 26.93 Fe₂O₃: 5.39 Na₂O: 0.59 BaO: 0.000 TiO₂: 0.50 MnO: 0.000 K₂O: 10.56</td>
<td>11.</td>
<td>Si: 3.312 Mg: 0.258 Ca: 0.010 Cr: 0.000 Al: 2.177 Fe₂: 0.309 Na: 0.035 Ba: 0.000 Ti: 0.026 Mn: 0.001 K: 0.928 Fc: 0.000</td>
<td>A(MUSC) = 0.4619702935 A(CELAD) = 0.1310410500 A(CELAD) = 0.0005771598</td>
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<tr>
<td>87-12</td>
<td>73</td>
<td>SiO₂: 47.36 MgO: 1.42 CaO: 0.000 Cr₂O₃: 0.000 Al₂O₃: 30.68 Fe₂O₃: 3.73 Na₂O: 1.04 BaO: 0.000 TiO₂: 0.30 MnO: 0.004 K₂O: 9.65</td>
<td>11.</td>
<td>Si: 3.219 Mg: 0.144 Ca: 0.000 Cr: 0.000 Al: 2.456 Fe₂: 0.212 Na: 0.137 Ba: 0.000 Ti: 0.015 Mn: 0.002 K: 0.437 Fc: 0.000</td>
<td>A(MUSC) = 0.538992296 A(CELAD) = 0.009013536 A(CELAD) = 0.0000000000</td>
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<td>87-12</td>
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<td>SiO₂: 48.43 MgO: 2.80 CaO: 0.03 Cr₂O₃: 0.000 Al₂O₃: 31.06 Fe₂O₃: 6.48 Na₂O: 1.41 BaO: 0.000 TiO₂: 0.34 MnO: 0.19 K₂O: 7.33</td>
<td>11.</td>
<td>Si: 3.052 Mg: 0.287 Ca: 0.002 Cr: 0.000 Al: 2.515 Fe₂: 0.372 Na: 0.188 Ba: 0.000 Ti: 0.018 Mn: 0.011 K: 0.642 Fc: 0.000</td>
<td>A(MUSC) = 0.426362298 A(CELAD) = 0.0092055464 A(CELAD) = 0.00012391642</td>
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**Total:** 94.01
ROCK NO. 86-53 MUSCOVITE ANAL NO. 57 MU b
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 48.01 MgO: 2.38 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 26.73 Fe₂O₃: 5.37 Na₂O: 0.30 BaO: 0.00
K₂O: 0.36 MnO: 0.01 Total: 93.86
MINERAL FORMULA NO. OF OXYGENS = 11.
Si: 3.32 Cr: 0.00 Al: 2.18 Ti: 0.019
O: 3.34 Mg: 0.246 Na: 0.048 K: 0.929 Fe₃: 0.00
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.44471017 A(CELA) = 0.1264094453
A(PARAG) = 0.0192757964 A(MARG) = 0.0000000000

ROCK NO. 86-53 CHLORITE ANAL NO. 58 CH 1
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 24.92 MgO: 14.12 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 20.12 Fe₂O₃: 26.29 Na₂O: 0.00 NiO: 0.00
K₂O: 0.07 MnO: 0.23 Total: 85.75
MINERAL FORMULA NO. OF OXYGENS = 14.
Si: 2.71 Mg: 2.28 Ca: 0.00 Al: 2.57 Ti: 0.006
Mg: 0.0021 Na: 0.0000 Ni: 0.0000 K: 0.0000 Fe₃: 0.0000
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(CLINOCL) = 0.0241750367

ROCK NO. 87-05 GARNET ANAL NO. 59 GT 1
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 37.37 MgO: 4.4b CaO: 8.21 Cr₂O₃: 0.01
Al₂O₃: 19.53 Fe₂O₃: 18.63 Na₂O: 0.00 BaO: 0.00
K₂O: 0.00 MnO: 15.27 Total: 99.48
MINERAL FORMULA NO. OF OXYGENS = 12.
Si: 3.03 Cr: 0.00 Al: 1.87 Fe₂: 1.21 Na: 0.0000
Mg: 0.0000 Mn: 0.0000 K: 0.0000 Fe₃: 0.0510
X_gr = 0.018 Xₚ = 0.346
Xₚₙ = 0.400 X_gr = 0.235

ROCK NO. 87-05 MUSCOVITE ANAL NO. 60 MU 1
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 47.61 MgO: 2.01 CaO: 0.03 Cr₂O₃: 0.00
Al₂O₃: 28.49 Fe₂O₃: 4.66 Na₂O: 0.53 BaO: 0.00
K₂O: 0.30 MnO: 0.03 Total: 93.69
MINERAL FORMULA NO. OF OXYGENS = 11.
Si: 3.275 Mg: 0.026 Cr: 0.0000
Al: 2.310 Fe₂: 0.268 Na: 0.071 Ba: 0.0000
Ti: 0.016 K: 0.0000 Fe₃: 0.0000
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.4815542102 A(CELA) = 0.0995641094
A(PARAG) = 0.0366740044 A(MARG) = 0.0000000000

ROCK NO. 87-05 MUSCOVITE ANAL NO. 61 MU 2
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 47.78 MgO: 1.9b CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 27.97 Fe₂O₃: 4.55 Na₂O: 0.54 BaO: 0.00
K₂O: 0.34 MnO: 0.01 Total: 93.28
MINERAL FORMULA NO. OF OXYGENS = 11.
Si: 3.300 Mg: 0.202 Ca: 0.0000 Cr: 0.0000
Al: 2.278 Fe₂: 0.263 Na: 0.072 Ba: 0.0000
Ti: 0.018 K: 0.893 Fe₃: 0.0000
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.4869590708 A(CELA) = 0.1075186729
A(PARAG) = 0.0343626291 A(MARG) = 0.0000000000

ROCK NO. 87-05 MUSCOVITE ANAL NO. 62 MU 3
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 47.74 MgO: 2.01 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 28.10 Fe₂O₃: 4.56 Na₂O: 0.53 BaO: 0.00
K₂O: 0.34 MnO: 0.00 Total: 93.56
MINERAL FORMULA NO. OF OXYGENS = 11.
Si: 3.291 Mg: 0.207 Ca: 0.0000 Cr: 0.0000
Al: 2.284 Fe₂: 0.263 Na: 0.071 Ba: 0.0000
Ti: 0.018 K: 0.904 Fe₃: 0.0000
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.9213365779 A(CELA) = 0.1097364905
A(PARAG) = 0.0356226990 A(MARG) = 0.0000000000

ROCK NO. 87-05 MUSCOVITE ANAL NO. 63 MU 4
WEIGHT-% OXIDES (FeC = Fe-TOTAL)
SiO₂: 47.78 MgO: 1.9b CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 27.97 Fe₂O₃: 4.55 Na₂O: 0.54 BaO: 0.00
K₂O: 0.34 MnO: 0.01 Total: 93.28
MINERAL FORMULA NO. OF OXYGENS = 11.
Si: 3.300 Mg: 0.202 Ca: 0.0000 Cr: 0.0000
Al: 2.278 Fe₂: 0.263 Na: 0.072 Ba: 0.0000
Ti: 0.018 K: 0.893 Fe₃: 0.0000
THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.4869590708 A(CELA) = 0.1075186729
A(PARAG) = 0.0343626291 A(MARG) = 0.0000000000
### Table: Mineral Analysis

<table>
<thead>
<tr>
<th>Rock No.</th>
<th>Mineral</th>
<th>Analytical No.</th>
<th>MU</th>
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<tr>
<td>ROCK NO - 87-22</td>
<td>MUSCOVITE</td>
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<td>ROCK NO - 87-22</td>
<td>CHLORITE</td>
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<tr>
<td>ROCK NO - 88-53</td>
<td>MUSCOVITE</td>
<td>56</td>
<td>5</td>
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</table>

#### WEIGHT-% OXIDES

- **SiO₂**: 48.65 - 48.77
- **MgO**: 2.61 - 2.33
- **Al₂O₃**: 27.23 - 27.30
- **Fe₂O₃**: 5.13 - 6.29
- **K₂O**: 0.02 - 0.01

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

- **A(MUSC)**: 0.4493684173
- **A(CELAD)**: 0.138218139
- **A(MUSC)**: 0.4349768192
- **A(CELAD)**: 0.0149625497
- **A(MUSC)**: 0.4359414901
- **A(CELAD)**: 0.1194625497

#### MINERAL FORMULA NO. OF OXYGENS

- **Si**: 3.316 - 3.375
- **Mg**: 0.265 - 0.243
- **Al**: 2.188 - 2.133
- **Fe**: 0.292 - 0.265
- **K**: 0.009 - 0.001

### Additional Data

- **SiO₂**: 49.12 - 48.77
- **MgO**: 2.87 - 0.02
- **Al₂O₃**: 26.08 - 2.33
- **Fe₂O₃**: 4.93 - 5.13
- **K₂O**: 0.02 - 0.01
- **Si**: 3.316 - 3.375
- **Mg**: 0.265 - 0.243
- **Al**: 2.188 - 2.133
- **Fe**: 0.292 - 0.265
- **K**: 0.009 - 0.001

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

- **A(MUSC)**: 0.1483439439
- **A(CELAD)**: 0.1527978412
- **A(MUSC)**: 0.1483439439
- **A(CELAD)**: 0.1483439439
- **A(MUSC)**: 0.1483439439
- **A(CELAD)**: 0.1483439439
- **A(MUSC)**: 0.1483439439
- **A(CELAD)**: 0.1483439439
- **A(MUSC)**: 0.1483439439
- **A(CELAD)**: 0.1483439439

#### Additional Information

- **ROCK NO - 86-53 MUSCOVITE ANAL NO - 53 MU 2**
- **ROCK NO - 86-53 MUSCOVITE ANAL NO - 55 MU 4**
- **ROCK NO - 86-53 MUSCOVITE ANAL NO - 56 MU 5**
- **ROCK NO - 86-53 MUSCOVITE ANAL NO - 56 MU 5**

---

**Note:** The table and data provided are extracted from a scientific document, likely related to mineralogy or petrology, presenting detailed chemical and thermodynamic analysis results. The data includes various oxides and their weight percentages, mineral formulas, and thermodynamic activities under specific conditions.
<table>
<thead>
<tr>
<th>Rock No.</th>
<th>Mineral Type</th>
<th>Anal No.</th>
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<th>[B]</th>
<th>[C]</th>
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<td>Mg</td>
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<td>Cr</td>
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<td>BIOTITE</td>
<td>ANAL NO. 43</td>
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<td>Ca</td>
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<td>ROCK NO. 66-50</td>
<td>BIOTITE</td>
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<td>Mg</td>
<td>Ca</td>
<td>Cr</td>
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<td>ROCK NO. 66-50</td>
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<td>ANAL NO. 45</td>
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<td>Mg</td>
<td>Ca</td>
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**WEIGHT-% OXIDES**

- **FeO** = Fe-TOTAL

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<tr>
<td>SiO₂</td>
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<tr>
<td>MgO</td>
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<tr>
<td>Al₂O₃</td>
<td>15.67</td>
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<tr>
<td>TiO₂</td>
<td>2.06</td>
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</tbody>
</table>

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 30.60 |
- **MgO** | 10.91 |
- **Al₂O₃** | 15.67 |
- **TiO₂** | 2.06 |

**MINERAL FORMULA NO. OF OXYGENS = 11.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(OH-PHLOG) = 0.0654874281 A(OH-ANN) = 0.0955262196

---

**ROCK NO. 87-22 | MUSCOVITE | ANAL NO. 46 | CH | 1**

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 48.72 |
- **MgO** | 2.73 |
- **CaO** | 0.00 |
- **Cr₂O₃** | 0.00 |
- **Fe₂O₃ (Total)** | 94.88 |

**MINERAL FORMULA NO. OF OXYGENS = 26.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(MUSC) = 0.1294338558 A(CELAD) = 0.1460462213 A(MARG) = 0.0000000000

---

**ROCK NO. 67-22 | MUSCOVITE | ANAL NO. 48 | MU | 4**

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 48.29 |
- **MgO** | 2.52 |
- **CaO** | 0.00 |
- **Cr₂O₃** | 0.00 |
- **Fe₂O₃ (Total)** | 94.85 |

**MINERAL FORMULA NO. OF OXYGENS = 26.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(MUSC) = 0.13460462213 A(CELAD) = 0.13460462213 A(MARG) = 0.0000000000

---

**ROCK NO. 87-22 | MUSCOVITE | ANAL NO. 47 | CH | 1**

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 27.56 |
- **MgO** | 12.14 |
- **CaO** | 0.00 |
- **Cr₂O₃** | 0.00 |
- **Fe₂O₃ (Total)** | 94.27 |

**MINERAL FORMULA NO. OF OXYGENS = 26.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(MUSC) = 0.3854921558 A(CELAD) = 0.1447109580 A(MARG) = 0.0000000000

---

**ROCK NO. 67-22 | MUSCOVITE | ANAL NO. 45 | MU | 4**

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 48.29 |
- **MgO** | 2.52 |
- **CaO** | 0.00 |
- **Cr₂O₃** | 0.00 |
- **Fe₂O₃ (Total)** | 94.85 |

**MINERAL FORMULA NO. OF OXYGENS = 26.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(MUSC) = 0.13460462213 A(CELAD) = 0.13460462213 A(MARG) = 0.0000000000

---

**ROCK NO. 87-22 | MUSCOVITE | ANAL NO. 44 | MU | 4**

**WEIGHT-% OXIDES (FeO = Fe-TOTAL)**

- **SiO₂** | 49.37 |
- **MgO** | 2.86 |
- **CaO** | 0.00 |
- **Cr₂O₃** | 0.00 |
- **Fe₂O₃ (Total)** | 94.93 |

**MINERAL FORMULA NO. OF OXYGENS = 26.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

- A(MUSC) = 0.4102141857 A(CELAD) = 0.1583842933 A(MARG) = 0.0000000000
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<th>MINERAL FORMULA</th>
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<th>WEIGHT-% OXIDES (FeC) = Fe-TOTAL</th>
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<tr>
<td>Biotite</td>
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<td>Chl</td>
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<td>Garnet</td>
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**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

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<th>Weight-% Oxides</th>
<th>Mineral Formula</th>
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**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

<table>
<thead>
<tr>
<th>Weight-% Oxides</th>
<th>Mineral Formula</th>
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<tbody>
<tr>
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<td>21.33</td>
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THERMODYNAMIC ACTIVITIES (ON-SITE MIXING MODEL)

A(MUSC) = 0.5105484515
A(CELAD) = 0.081395705
A(MARG) = 0.0000000000

MINERAL FORMULA NO. OF OXYGENS = 11.

Si : 2.658 Mg : 2.118 Ca : 0.000 Cr : 0.000
Al : 2.850 Fe2: 2.535 Na : 0.000 Ni : 0.000
Ti : 0.008 Mn:0.040 K : 0.000 Fe3 : 0.000

THERMODYNAMIC ACTIVITIES (ON-SITE MIXING MODEL)

A(CLINOC) = 0.0162541047

MINERAL FORMULA NO. OF OXYGENS = 11.

Si : 2.667 Mg : 2.028 Ca : 0.000 Cr : 0.000
Al : 2.864 Fe2: 2.596 Na : 0.000 Ni : 0.000
Ti : 0.004 Mn:0.036 K : 0.000 Fe3 : 0.000

THERMODYNAMIC ACTIVITIES (ON-SITE MIXING MODEL)

A(CLINOCL) = 0.0148364380

ROCK NO - 87-06 CHLORITE ANAL NO - 17 CG CH

WEIGHT-% OXIDES ( FeO = Fe-TOTAL )

SiO2 : 24.51 MgO: 13.12 CaO : 0.00 Cr2O3: 0.00
Al2O3: 20.76 FeO: 27.94 Na2O: 0.00 NiO : 0.00
TiO2 : 0.10 MnO: 0.44 K2O : 0.00 Total: 86.95

MINERAL FORMULA NO. OF OXYGENS = 14.

Si : 2.634 Mg : 2.081 Ca : 0.000 Cr : 0.000
Al : 2.861 Fe2: 2.582 Na : 0.000 Ni : 0.000
Ti : 0.006 Mn:0.034 K : 0.000 Fe3 : 0.000

THERMODYNAMIC ACTIVITIES (ON-SITE MIXING MODEL)

A(CLINOC) = 0.014363400
ROCK NO. 87-11  GARNET  ANAL NO.- 2  GT CG 2
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 36.87 MgO: 0.58 CaO: 6.55 Cr₂O₃: 0.01
Al₂O₃: 19.38 FeO: 18.53 Na₂O: 0.05 BaO: 0.00
TiO₂: 0.14 MnO: 16.01 K₂O: 0.00 Total: 98.62
MINERAL FORMULA  NO. OF OXYGENS = 12.
Si : 3.026 Mg : 0.071 Ca : 0.585 Cr : 0.001
Al : 1.875 Fe₂: 1.208 Na : 0.008 Ba : 0.000
Ti : 0.009 Mn: 1.155 K : 0.000 Fe₃: 0.064

ROCK NO. 87-11  GARNET  ANAL NO.- 3  CG GT 3
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 37.76 MgO: 0.71 CaO: 6.48 Cr₂O₃: 0.02
Al₂O₃: 19.68 FeO: 21.77 Na₂O: 0.02 BaO: 0.000
TiO₂: 0.06 MnO: 14.08 K₂O: 0.00 Total: 100.76
MINERAL FORMULA  NO. OF OXYGENS = 12.
Si : 3.038 Mg : 0.085 Ca : 0.559 Cr : 0.001
Al : 1.866 Fe₂: 1.432 Na : 0.003 Ba : 0.000
Ti : 0.004 Mn: 0.469 K : 0.000 Fe₃: 0.033

ROCK NO. 87-11  MUSCOVITE  ANAL NO.- 5  CG MU 1
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 47.42 MgO: 1.41 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 30.30 FeO: 4.31 Na₂O: 1.03 BaO: 0.000
TiO₂: 0.30 MnO: 0.02 K₂O: 9.73 Total: 94.52
MINERAL FORMULA  NO. OF OXYGENS = 11.
Si : 3.221 Mg : 0.143 Ca : 0.000 Cr : 0.000
Al : 2.429 Fe₂: 0.245 Na : 0.126 Ba : 0.000
Ti : 0.015 Mn: 0.001 K : 0.844 Fe₃: 0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.5322548714 A(CELAD) = 0.007686739
A(PARAG) = 0.0841853023 A(MARG) = 0.0000000000

ROCK NO. 87-11  CHLORITE  ANAL NO.- 6  CH CG 1
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 24.73 MgO: 13.87 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 20.95 FeO: 24.94 Na₂O: 0.00 NiO: 0.00
TiO₂: 0.07 MnO: 0.78 K₂O: 0.00 Total: 85.34
MINERAL FORMULA  NO. OF OXYGENS = 14.
Si : 2.866 Mg : 2.247 Ca : 0.000 Cr : 0.000
Al : 2.685 Fe₂: 2.267 Na : 0.000 Ni : 0.000
Ti : 0.066 Mn: 0.072 K : 0.000 Fe₃: 0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(CLINOC) = 0.023419229

ROCK NO. 87-11  MAGNETITE  ANAL NO.- 7  CG MT 1
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 0.07 MgO: 0.02 CaO: 0.00 Cr₂O₃: 0.05
Al₂O₃: 0.04 FeO: 75.19 Na₂O: 0.00 BaO: 0.00
TiO₂: 17.39 MnO: 0.74 K₂O: 0.00 Total: 93.50
MINERAL FORMULA  NO. OF OXYGENS = 4.
Si : 0.003 Mg : 0.001 Ca : 0.000 Cr : 0.002
Al : 0.002 Fe₂: 1.446 Na : 0.000 Ba : 0.000
Ti : 0.511 Mn: 0.024 K : 0.000 Fe₃: 0.006

ROCK NO. 87-06  GARNET  ANAL NO.- 8  CG GT 2
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 37.30 MgO: 0.82 CaO: 0.40 Cr₂O₃: 0.02
Al₂O₃: 19.97 FeO: 21.91 Na₂O: 0.00 BaO: 0.000
TiO₂: 0.20 MnO: 13.12 K₂O: 0.00 Total: 94.60
MINERAL FORMULA  NO. OF OXYGENS = 12.
Si : 3.025 Mg : 0.099 Ca : 0.558 Cr : 0.001
Al : 1.909 Fe₂: 1.462 Na : 0.009 Ba : 0.000
Ti : 0.012 Mn: 0.001 K : 0.000 Fe₃: 0.024

ROCK NO. 87-06  MUSCOVITE  ANAL NO.- 9  CG MU 2
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 37.50 MgO: 0.54 CaO: 7.64 Cr₂O₃: 0.00
Al₂O₃: 20.08 FeO: 18.34 Na₂O: 0.00 BaO: 0.000
TiO₂: 0.15 MnO: 15.98 K₂O: 0.00 Total: 100.33
MINERAL FORMULA  NO. OF OXYGENS = 12.
Si : 3.021 Mg : 0.065 Ca : 0.643 Cr : 0.000
Al : 1.907 Fe₂: 1.963 Na : 0.009 Ba : 0.000
Ti : 0.009 Mn: 1.093 K : 0.000 Fe₃: 0.043

ROCK NO. 87-06  CHLORITE  ANAL NO.- 11  CH CG 1
WEIGHT-% OXIDES (FeO = Fe-TOTAL)
SiO₂: 47.56 MgO: 1.54 CaO: 0.00 Cr₂O₃: 0.00
Al₂O₃: 30.48 FeO: 4.29 Na₂O: 0.52 BaO: 0.000
TiO₂: 0.46 MnO: 0.03 K₂O: 10.39 Total: 95.27
MINERAL FORMULA  NO. OF OXYGENS = 11.
Si : 3.214 Mg : 0.155 Ca : 0.000 Cr : 0.000
Al : 2.429 Fe₂: 0.242 Na : 0.008 BA : 0.000
Ti : 0.023 Mn: 0.002 K : 0.886 Fe₃: 0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.5457947915 A(CELAD) = 0.0742353201
A(PARAG) = 0.0415153809 A(MARG) = 0.0000000000
SiO₂ : 43.71  MgO: 3.90  CaO : 0.00  Cr₂O₃: 0.00
Al₂O₃: 29.91  FeO: 7.66  Na₂O: 0.50  BaO : 0.00
TiO₂ : 0.33  MnO: 0.07  K₂O : 7.29  Total:93.57

MINERAL FORMULA: NO. OF OXYGENS = 11.
Si : 0.036  Mg:0.394  Ca :0.000  Cr :0.000
Al : 2.449  Fe2:0.157  Na: 0.067  Ba :0.000
Ti : 0.017  Mn: 0.004  K :0.464  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.2253686786 
A(PARAG) = 0.0234928243

ROCK NO- 85-23  MUSCOVITE ANAL NO- 1
WEIGHT-% OXIDES ( FeO = Fe-TOTAL)
SiO₂ : 24.81  MgO: 11.51  CaO : 0.02  Cr₂O₃: 0.00
Al₂O₃: 20.17  FeO:0.20.30  Na₂O: 0.03  BaO : 0.00
TiO₂ : 0.08  MnO: 0.27  K₂O : 0.04  Total:87.11

Si : 2.712  Mg:1.875  Ca :0.002  Cr :0.000
Al : 2.590  Fe2:0.760  Na: 0.006  Ba :0.000
Ti : 0.005  Mn: 0.025  K :0.000  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(CLINO) = 0.0590529807

ROCK NO- 85-23  CHLORITE ANAL NO- 1
WEIGHT-% OXIDES ( FeO = Fe-TOTAL)
SiO₂ : 24.92  MgO: 11.78  CaO : 0.00  Cr₂O₃: 0.00
Al₂O₃: 20.74  FeO:29.60  Na₂O: 0.04  BaO : 0.00
TiO₂ : 0.07  MnO: 0.34  K₂O : 0.02  Total:87.51

Si : 2.690  Mg:1.901  Ca :0.000  Cr :0.000
Al : 2.848  Fe2:2.681  Na: 0.008  Ba :0.000
Ti : 0.006  Mn: 0.031  K :0.003  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(CLINO) = 0.0048753832

ROCK NO- 85-23  CHLORITE ANAL NO- 2
WEIGHT-% OXIDES ( FeO = Fe-TOTAL)
SiO₂ : 24.85  MgO:12.45  CaO :0.00  Cr₂O₃: 0.00
Al₂O₃: 20.50  FeO:28.26  Na₂O: 0.01  BaO : 0.00
TiO₂ : 0.06  MnO: 0.28  K₂O : 0.00  Total:93.53

Si : 2.705  Mg:2.020  Ca :0.000  Cr :0.000
Al : 2.631  Fe2:2.582  Na: 0.002  Ba :0.000
Ti : 0.007  Mn: 0.026  K :0.000  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(CLINO) = 0.013320918

ROCK NO- 85-25  MUSCOVITE ANAL NO- 1
WEIGHT-% OXIDES ( FeO = Fe-TOTAL)
SiO₂ : 48.22  MgO: 1.83  CaO : 0.01  Cr₂O₃: 0.00
Al₂O₃: 29.86  FeO: 3.12  Na₂O: 0.63  BaO : 0.00
TiO₂ : 0.31  MnO: 0.01  K₂O :10.28  Total:94.27

MINERAL FORMULA: NO. OF OXYGENS = 11.
Si : 3.289  Mg:0.185  Ca :0.001  Cr :0.000
Al : 2.387  Fe2:0.177  Na: 0.083  Ba :0.000
Ti : 0.016  Mn: 0.001  K :0.889  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(MUSC) = 0.5567035079 
A(PARAG) = 0.0518523122
A(MARG) = 0.0001715217

ROCK NO- 85-25  BIOTITE ANAL NO- 2
WEIGHT-% OXIDES ( FeO = Fe-TOTAL)
SiO₂ : 36.85  MgO: 7.93  CaO : 0.02  Cr₂O₃: 0.00
Al₂O₃: 19.04  FeO:19.95  Na₂O: 0.15  F : 0.00
TiO₂ : 1.71  MnO: 0.15  K₂O :7.95  Total:93.73

MINERAL FORMULA: NO. OF OXYGENS = 11.
Si : 2.819  Mg:0.904  Ca :0.002  Cr :0.000
Al : 1.717  Fe2:1.276  Na: 0.022  F : 0.000
Ti : 0.048  Mn: 0.010  K :0.774  Fe3 :0.000

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)
A(OH-PHLOG) = 0.0204813220 
A(OH-ANN) = 0.0576209440
### ROCK NO. - 85-25 . MUSCOVITE

#### ANAL NO. - 1

**WEIGHT-% OXIDES** (Fe₂O₃ = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.18</td>
<td>1.59</td>
<td>0.01</td>
<td>0.00</td>
<td>6.09</td>
<td>2.94</td>
<td>0.68</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.41</td>
<td>MnO</td>
<td>0.60</td>
<td>K₂O</td>
<td>0.10</td>
<td>Total:93.79</td>
<td></td>
</tr>
</tbody>
</table>

#### MINERAL FORMULA

**NO. OF OXYGENS = 11.**

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.321</td>
<td>0.01</td>
<td>0.001</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

**A(MUSC) = 0.5779626800**

**A(CELAD) = 0.0819821358**

**A(MARG) = 0.0000200884**

### ROCK NO. - 85-25 . CHLORITE

#### ANAL NO. - 1

**WEIGHT-% OXIDES** (Fe₂O₃ = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.18</td>
<td>6.54</td>
<td>0.00</td>
<td>0.00</td>
<td>12.88</td>
<td>14.42</td>
<td>0.14</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.03</td>
<td>MnO</td>
<td>0.10</td>
<td>K₂O</td>
<td>1.92</td>
<td>Total:95.14</td>
<td></td>
</tr>
</tbody>
</table>

#### MINERAL FORMULA

**NO. OF OXYGENS = 14.**

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.040</td>
<td>0.830</td>
<td>0.000</td>
<td>0.00</td>
<td>1.291</td>
<td>1.027</td>
<td>0.0023</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

**A(CLINOC) = 0.018344433**

### ROCK NO. - 85-25 . CHLORITE

#### ANAL NO. - 2

**WEIGHT-% OXIDES** (Fe₂O₃ = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.71</td>
<td>13.11</td>
<td>0.00</td>
<td>0.00</td>
<td>20.65</td>
<td>27.16</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.06</td>
<td>MnO</td>
<td>0.20</td>
<td>K₂O</td>
<td>0.02</td>
<td>Total:85.99</td>
<td></td>
</tr>
</tbody>
</table>

#### MINERAL FORMULA

**NO. OF OXYGENS = 14.**

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.691</td>
<td>2.128</td>
<td>0.000</td>
<td>0.00</td>
<td>2.52</td>
<td>2.474</td>
<td>0.017</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

**A(CLINOC) = -0.0007505631**

### ROCK NO. - 85-25 . CHLORITE

#### ANAL NO. - 3

**WEIGHT-% OXIDES** (Fe₂O₃ = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.23</td>
<td>1.94</td>
<td>0.00</td>
<td>0.00</td>
<td>39.22</td>
<td>2.96</td>
<td>0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.28</td>
<td>MnO</td>
<td>0.00</td>
<td>K₂O</td>
<td>0.74</td>
<td>Total:93.81</td>
<td></td>
</tr>
</tbody>
</table>

#### MINERAL FORMULA

**NO. OF OXYGENS = 11.**

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.241</td>
<td>0.197</td>
<td>0.000</td>
<td>0.00</td>
<td>2.351</td>
<td>0.164</td>
<td>0.058</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

#### THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

**A(MUSC) = 0.579410352**

**A(CELAD) = 0.1273624897**

**A(MARG) = 0.0000000000**

---

**Note:** The table above represents the chemical composition and thermodynamic activities of different mineral species present in the rock samples, with columns for SiO₂, MgO, CaO, Cr₂O₃, Al₂O₃, Fe₂O₃, Na₂O, and BaO. The mineral formula and total oxygen count are also provided for each sample.
<table>
<thead>
<tr>
<th>ROCK NO</th>
<th>-71-4</th>
<th>MUSCOVITE</th>
<th>ANAL NO- 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES ( FeO = Fe-TOTAL )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ : 58.44</td>
<td>MgO : 2.02</td>
<td>CaO : 0.01</td>
<td>Cr₂O₃ : 0.00</td>
</tr>
<tr>
<td>Al₂O₃ : 29.37</td>
<td>FeO : 3.08</td>
<td>Na₂O : 0.49</td>
<td>BaO : 0.00</td>
</tr>
<tr>
<td>TiO₂ : 0.31</td>
<td>MnO : 0.00</td>
<td>K₂O : 0.10</td>
<td>Total: 94.25</td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 11.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si : 3.288</td>
<td>Mg : 0.204</td>
<td>Ca : 0.001</td>
<td>Cr : 0.000</td>
</tr>
<tr>
<td>Al : 2.359</td>
<td>Fe₂ : 0.175</td>
<td>Na : 0.004</td>
<td>Ba : 0.000</td>
</tr>
<tr>
<td>Ti : 0.016</td>
<td>Mn : 0.000</td>
<td>K : 0.012</td>
<td>Fe₃ : 0.000</td>
</tr>
</tbody>
</table>

THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)

A(MUSC) = 0.554356m492 A(CELAD) = 0.1230841270
A(PARAG) = 0.0392062925 A(MARG) = 0.000166923

<table>
<thead>
<tr>
<th>ROCK NO</th>
<th>-71-4</th>
<th>GARNET</th>
<th>ANAL NO- 2</th>
<th>Garnet Rim</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES ( FeO = Fe-TOTAL )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ : 37.41</td>
<td>MgO : 0.64</td>
<td>CaO : 0.94</td>
<td>Cr₂O₃ : 0.03</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ : 21.04</td>
<td>FeO : 28.02</td>
<td>Na₂O : 0.00</td>
<td>ZnO : 0.00</td>
<td></td>
</tr>
<tr>
<td>TiO₂ : 0.18</td>
<td>MnO : 0.36</td>
<td>K₂O : 0.00</td>
<td>Total: 100.32</td>
<td></td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si : 2.995</td>
<td>Mg : 0.076</td>
<td>Ca : 0.187</td>
<td>Cr : 0.002</td>
<td></td>
</tr>
<tr>
<td>Al : 1.406</td>
<td>Fe₂ : 1.167</td>
<td>Na : 0.000</td>
<td>Zn : 0.000</td>
<td></td>
</tr>
<tr>
<td>Ti : 0.011</td>
<td>Mn : 0.228</td>
<td>K : 0.000</td>
<td>Fe₃ : 0.001</td>
<td></td>
</tr>
</tbody>
</table>

Xₚᵧ = 0.028 Xₛₚ = 0.075
Xₐₘ = 0.624 X.grp = 0.275

<table>
<thead>
<tr>
<th>ROCK NO</th>
<th>-71-4</th>
<th>GARNET</th>
<th>ANAL NO- 3</th>
<th>Garnet Rim</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES ( FeO = Fe-TOTAL )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ : 37.22</td>
<td>MgO : 0.64</td>
<td>CaO : 0.97</td>
<td>Cr₂O₃ : 0.02</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃ : 20.92</td>
<td>FeO : 27.79</td>
<td>Na₂O : 0.00</td>
<td>ZnO : 0.00</td>
<td></td>
</tr>
<tr>
<td>TiO₂ : 0.17</td>
<td>MnO : 0.37</td>
<td>K₂O : 0.00</td>
<td>Total: 100.01</td>
<td></td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si : 2.990</td>
<td>Mg : 0.077</td>
<td>Ca : 0.185</td>
<td>Cr : 0.001</td>
<td></td>
</tr>
<tr>
<td>Al : 1.482</td>
<td>Fe₂ : 1.852</td>
<td>Na : 0.000</td>
<td>Zn : 0.000</td>
<td></td>
</tr>
<tr>
<td>Ti : 0.010</td>
<td>Mn : 0.257</td>
<td>K : 0.000</td>
<td>Fe₃ : 0.016</td>
<td></td>
</tr>
</tbody>
</table>

Xₚᵧ = 0.026 Xₛₚ = 0.085
Xₐₘ = 0.619 X.grp = 0.27

<table>
<thead>
<tr>
<th>ROCK NO</th>
<th>-71-4</th>
<th>MUSCOVITE</th>
<th>ANAL NO- 1</th>
<th>Garnet Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES ( FeO = Fe-TOTAL )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ : 37.69</td>
<td>MgO : 0.55</td>
<td>CaO : 0.10</td>
<td>Cr₂O₃ : 0.00</td>
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</tr>
<tr>
<td>Al₂O₃ : 21.17</td>
<td>FeO : 25.78</td>
<td>Na₂O : 0.00</td>
<td>ZnO : 0.00</td>
<td></td>
</tr>
<tr>
<td>TiO₂ : 0.00</td>
<td>MnO : 5.01</td>
<td>K₂O : 0.00</td>
<td>Total: 100.48</td>
<td></td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si : 3.000</td>
<td>Mg : 0.965</td>
<td>Ca : 0.879</td>
<td>Cr : 0.000</td>
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</tr>
<tr>
<td>Al : 1.941</td>
<td>Fe₂ : 1.720</td>
<td>Na : 0.000</td>
<td>Zn : 0.000</td>
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</tr>
<tr>
<td>Ti : 0.000</td>
<td>Mn : 0.338</td>
<td>K : 0.000</td>
<td>Fe₃ : 0.000</td>
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</tr>
</tbody>
</table>

Xₚᵧ = 0.024 Xₛₚ = 0.114
Xₐₘ = 0.574 X.grp = 0.293

00 456
<table>
<thead>
<tr>
<th>ROCK NO.</th>
<th>MINERAL FORMULA</th>
<th>NO. OF OXYGENS</th>
<th>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77-101</td>
<td>TiC, Sb</td>
<td>45.76</td>
<td>MgO: 1.88, CaO: 0.00, Cr₂O₃: 0.00</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 30.26</td>
<td></td>
<td>Fe₂O₃: 2.71, Na₂O: 0.59, BaO: 0.00</td>
</tr>
<tr>
<td></td>
<td>TiO₂: 0.44</td>
<td></td>
<td>MnO: 0.00, K₂O: 0.18, Total: 94.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MINERAL FORMULA NO. OF OXYGENS: 11.</td>
</tr>
<tr>
<td>Si</td>
<td>3.185</td>
<td></td>
<td>Mg: 0.195, Ca: 0.000, Cr: 0.000</td>
</tr>
<tr>
<td>Al</td>
<td>2.491</td>
<td></td>
<td>Fe₂: 0.158, Na: 0.080, Ba: 0.000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.026</td>
<td></td>
<td>Mn: 0.000, K: 0.901, Fe₃: 0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)</td>
</tr>
<tr>
<td></td>
<td>A(MUSC): 0.5835829377</td>
<td></td>
<td>A(CELAD): 0.0948179860</td>
</tr>
<tr>
<td></td>
<td>A(PARAG): 0.0511570492</td>
<td></td>
<td>A(MARG): 0.0000000000</td>
</tr>
<tr>
<td>77-101</td>
<td>TiC, Sb</td>
<td>44.47</td>
<td>MgO: 1.88, CaO: 0.00, Cr₂O₃: 0.00</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 30.26</td>
<td></td>
<td>Fe₂O₃: 2.77, Na₂O: 0.46, BaO: 0.00</td>
</tr>
<tr>
<td></td>
<td>TiO₂: 0.44</td>
<td></td>
<td>MnO: 0.000, K₂O: 0.10, Total: 94.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MINERAL FORMULA NO. OF OXYGENS: 11.</td>
</tr>
<tr>
<td>Si</td>
<td>3.237</td>
<td></td>
<td>Mg: 0.202, Ca: 0.000, Cr: 0.000</td>
</tr>
<tr>
<td>Al</td>
<td>2.424</td>
<td></td>
<td>Fe₂: 0.157, Na: 0.081, Ba: 0.000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.022</td>
<td></td>
<td>Mn: 0.000, K: 0.941, Fe₃: 0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)</td>
</tr>
<tr>
<td></td>
<td>A(MUSC): 0.5759525511</td>
<td></td>
<td>A(CELAD): 0.1107273698</td>
</tr>
<tr>
<td></td>
<td>A(PARAG): 0.0383125581</td>
<td></td>
<td>A(MARG): 0.0000000000</td>
</tr>
<tr>
<td>84-1</td>
<td>TiC, Sb</td>
<td>45.76</td>
<td>MgO: 1.88, CaO: 0.00, Cr₂O₃: 0.00</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 30.26</td>
<td></td>
<td>Fe₂O₃: 2.77, Na₂O: 0.46, BaO: 0.00</td>
</tr>
<tr>
<td></td>
<td>TiO₂: 0.44</td>
<td></td>
<td>MnO: 0.000, K₂O: 0.10, Total: 94.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MINERAL FORMULA NO. OF OXYGENS: 11.</td>
</tr>
<tr>
<td>Si</td>
<td>3.237</td>
<td></td>
<td>Mg: 0.202, Ca: 0.000, Cr: 0.000</td>
</tr>
<tr>
<td>Al</td>
<td>2.424</td>
<td></td>
<td>Fe₂: 0.157, Na: 0.081, Ba: 0.000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.022</td>
<td></td>
<td>Mn: 0.000, K: 0.941, Fe₃: 0.000</td>
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<tr>
<td></td>
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<td></td>
<td>THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)</td>
</tr>
<tr>
<td></td>
<td>A(OH-PHLOG): 0.0314445048a A(OH-ANN): 0.0788805485</td>
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<td></td>
</tr>
<tr>
<td>84-4</td>
<td>Biotite</td>
<td>45.76</td>
<td>MgO: 1.88, CaO: 0.00, Cr₂O₃: 0.00</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 30.26</td>
<td></td>
<td>Fe₂O₃: 2.77, Na₂O: 0.46, BaO: 0.00</td>
</tr>
<tr>
<td></td>
<td>TiO₂: 0.44</td>
<td></td>
<td>MnO: 0.000, K₂O: 0.10, Total: 94.09</td>
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<tr>
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<td>MINERAL FORMULA NO. OF OXYGENS: 11.</td>
</tr>
<tr>
<td>Si</td>
<td>3.237</td>
<td></td>
<td>Mg: 0.202, Ca: 0.000, Cr: 0.000</td>
</tr>
<tr>
<td>Al</td>
<td>2.424</td>
<td></td>
<td>Fe₂: 0.157, Na: 0.081, Ba: 0.000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.022</td>
<td></td>
<td>Mn: 0.000, K: 0.941, Fe₃: 0.000</td>
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<tr>
<td></td>
<td>A(OH-PHLOG): 0.0314445048a A(OH-ANN): 0.0788805485</td>
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<tr>
<td>84-4</td>
<td>Magnetite</td>
<td>45.76</td>
<td>MgO: 1.88, CaO: 0.00, Cr₂O₃: 0.00</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 30.26</td>
<td></td>
<td>Fe₂O₃: 2.77, Na₂O: 0.46, BaO: 0.00</td>
</tr>
<tr>
<td></td>
<td>TiO₂: 0.44</td>
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<td>MnO: 0.000, K₂O: 0.10, Total: 94.09</td>
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<td></td>
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<td></td>
<td>MINERAL FORMULA NO. OF OXYGENS: 11.</td>
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<tr>
<td>Si</td>
<td>3.237</td>
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<td>Mg: 0.202, Ca: 0.000, Cr: 0.000</td>
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<tr>
<td>Al</td>
<td>2.424</td>
<td></td>
<td>Fe₂: 0.157, Na: 0.081, Ba: 0.000</td>
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<tr>
<td>Ti</td>
<td>0.022</td>
<td></td>
<td>Mn: 0.000, K: 0.941, Fe₃: 0.000</td>
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<td>THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)</td>
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<td>A(OH-PHLOG): 0.0314445048a A(OH-ANN): 0.0788805485</td>
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<td>ROCK NO.</td>
<td>85-12</td>
<td>CHLORITE</td>
<td>ANAL NO.: 9</td>
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<td>SiO₂</td>
<td>24.99</td>
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<td>Fe₂O₃: 3.16</td>
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<td>TiO₂</td>
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<td>MnO: 0.36</td>
<td>K₂O: 0.03</td>
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<tr>
<td>Si</td>
<td>2.625</td>
<td>Mg: 1.922</td>
<td>Ca: 0.008</td>
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<td>Al</td>
<td>2.760</td>
<td>Fe₂: 2.607</td>
<td>Na: 0.008</td>
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<td>Ti</td>
<td>0.009</td>
<td>Mn: 0.035</td>
<td>K: 0.000</td>
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**Thermodynamic Activities (On-Sites Mixing Model):**

A(CLINO(CL)) = 0.0108618867

<table>
<thead>
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<th>ROCK NO.</th>
<th>85-12</th>
<th>MUSCovITE</th>
<th>ANAL NO.: 10</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>44.83</td>
<td>Mgo: 3.02</td>
<td>CaO: 0.00</td>
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<tr>
<td>Al₂O₃</td>
<td>28.96</td>
<td>Fe₂O₃: 6.48</td>
<td>Na₂O: 0.50</td>
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<tr>
<td>TiO₂</td>
<td>0.23</td>
<td>MnO: 0.07</td>
<td>K₂O: 9.20</td>
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<tr>
<td>Si</td>
<td>3.130</td>
<td>Mg: 0.314</td>
<td>Ca: 0.000</td>
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<tr>
<td>Al</td>
<td>2.384</td>
<td>Fe₂: 0.378</td>
<td>Na: 0.066</td>
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<tr>
<td>Ti</td>
<td>0.012</td>
<td>Mn: 0.004</td>
<td>K: 0.819</td>
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</tbody>
</table>

**Thermodynamic Activities (On-Sites Mixing Model):**

A(MUSC) = 0.3605508804
A(CELAD) = 0.0771133004
A(PARAG) = 0.0297815874
A(MARG) = 0.0000000000

<table>
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<tr>
<th>ROCK NO.</th>
<th>85-12</th>
<th>MUSCovITE</th>
<th>ANAL NO.: 11</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.29</td>
<td>Mgo: 1.81</td>
<td>CaO: 0.00</td>
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<tr>
<td>Al₂O₃</td>
<td>30.35</td>
<td>Fe₂O₃: 2.89</td>
<td>Na₂O: 0.59</td>
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<td>TiO₂</td>
<td>0.26</td>
<td>MnO: 0.02</td>
<td>K₂O: 10.37</td>
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<tr>
<td>Si</td>
<td>3.254</td>
<td>Mg: 0.182</td>
<td>Ca: 0.000</td>
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<tr>
<td>Al</td>
<td>2.424</td>
<td>Fe₂: 0.163</td>
<td>Na: 0.077</td>
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<tr>
<td>Ti</td>
<td>0.013</td>
<td>Mn: 0.001</td>
<td>K: 0.841</td>
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</table>

**Thermodynamic Activities (On-Sites Mixing Model):**

A(MUSC) = 0.5752173594
A(CELAD) = 0.1024861336
A(PARAG) = 0.0487400723
A(MARG) = 0.0000000000

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<table>
<thead>
<tr>
<th>ROCK NO.</th>
<th>85-12</th>
<th>BIOTITE</th>
<th>ANAL NO.: 15</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>34.95</td>
<td>Mgo: 8.36</td>
<td>CaO: 0.01</td>
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<tr>
<td>Al₂O₃</td>
<td>18.12</td>
<td>Fe₂O₃: 2.91</td>
<td>Na₂O: 0.11</td>
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<tr>
<td>TiO₂</td>
<td>1.79</td>
<td>MnO: 0.24</td>
<td>K₂O: 0.14</td>
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<tr>
<td>Si</td>
<td>3.752</td>
<td>Mg: 0.981</td>
<td>Ca: 0.001</td>
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<tr>
<td>Al</td>
<td>1.682</td>
<td>Fe₂: 1.45</td>
<td>Na: 0.017</td>
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<tr>
<td>Ti</td>
<td>0.106</td>
<td>Mn: 0.016</td>
<td>K: 0.017</td>
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</tbody>
</table>

**Thermodynamic Activities (On-Sites Mixing Model):**

A(OH-PHLOG) = 0.0201696476
A(OH-ANN) = 0.0832641677

---

<table>
<thead>
<tr>
<th>ROCK NO.</th>
<th>85-12</th>
<th>BIOTITE</th>
<th>ANAL NO.: 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>36.18</td>
<td>Mgo: 8.41</td>
<td>CaO: 0.01</td>
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<tr>
<td>Al₂O₃</td>
<td>17.48</td>
<td>Fe₂O₃: 2.18</td>
<td>Na₂O: 0.11</td>
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<tr>
<td>TiO₂</td>
<td>1.86</td>
<td>MnO: 0.22</td>
<td>K₂O: 0.45</td>
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<tr>
<td>Si</td>
<td>3.791</td>
<td>Mg: 0.967</td>
<td>Ca: 0.001</td>
</tr>
<tr>
<td>Al</td>
<td>1.590</td>
<td>Fe₂: 1.40</td>
<td>Na: 0.016</td>
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<tr>
<td>Ti</td>
<td>0.109</td>
<td>Mn: 0.014</td>
<td>K: 0.032</td>
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</table>

**Thermodynamic Activities (On-Sites Mixing Model):**

A(OH-PHLOG) = 0.0265781200
A(OH-ANN) = 0.0831234175
<table>
<thead>
<tr>
<th>ROCK NO - 85-12</th>
<th>Biotite</th>
<th>ANAL NO - 17</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;: 36.34</td>
<td>MgO: 8.37</td>
<td>CaO: 0.00</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 17.57</td>
<td>FeO: 22.41</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.08</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 1.81</td>
<td>MnO: 0.22</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 7.97</td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 11.</td>
<td></td>
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| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(OH-PHLOG): 0.024588570 | A(OH-ANN): 0.0633006534 |

<table>
<thead>
<tr>
<th>ROCK NO - 85-12</th>
<th>Garnet</th>
<th>ANAL NO - 19</th>
<th>EDGE 2</th>
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</thead>
<tbody>
<tr>
<td><strong>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;: 32.75</td>
<td>MgO: 5.98</td>
<td>CaO: 0.00</td>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 0.00</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 17.57</td>
<td>FeO: 28.58</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
<td>F: 0.00</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 0.04</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 6.78</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;: 0.00</td>
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<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
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<table>
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<th>Garnet</th>
<th>ANAL NO - 20</th>
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<tbody>
<tr>
<td><strong>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</strong></td>
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<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;: 34.73</td>
<td>MgO: 0.60</td>
<td>CaO: 8.62</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 19.57</td>
<td>FeO: 22.78</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 8.08</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
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<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
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<tr>
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<th>Garnet</th>
<th>ANAL NO - 21</th>
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<tbody>
<tr>
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<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;: 36.34</td>
<td>MgO: 0.50</td>
<td>CaO: 8.74</td>
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<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 20.70</td>
<td>FeO: 21.77</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
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<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 11.50</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
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<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
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Rocks with similar compositions and mineral associations are listed below:

**ROCK NO - 85-12**

- **Biotite**: WEIGHT-% OXIDES (FeO = Fe-TOTAL)

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<thead>
<tr>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;: 36.34</th>
<th>MgO: 8.37</th>
<th>CaO: 0.00</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 0.00</th>
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</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 17.57</td>
<td>FeO: 22.41</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.08</td>
<td>F: 0.00</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 1.81</td>
<td>MnO: 0.22</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 7.97</td>
<td>Total: 94.77</td>
</tr>
<tr>
<td>MINERAL FORMULA NO. OF OXYGENS = 11.</td>
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**ROCK NO - 85-12**

- **Garnet**: WEIGHT-% OXIDES (FeO = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;: 32.75</th>
<th>MgO: 5.98</th>
<th>CaO: 0.00</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 17.57</td>
<td>FeO: 28.58</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
<td>F: 0.00</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 0.04</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 6.78</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;: 0.00</td>
</tr>
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<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
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**ROCK NO - 85-12**

- **Garnet**: WEIGHT-% OXIDES (FeO = Fe-TOTAL)

<table>
<thead>
<tr>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;: 34.73</th>
<th>MgO: 0.60</th>
<th>CaO: 8.62</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 19.57</td>
<td>FeO: 22.78</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
<td>ZnO: 0.00</td>
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<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 8.08</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
<td>Total: 95.10</td>
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<td>MINERAL FORMULA NO. OF OXYGENS = 12.</td>
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- **Garnet**: WEIGHT-% OXIDES (FeO = Fe-TOTAL)

<table>
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<tr>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;: 36.34</th>
<th>MgO: 0.50</th>
<th>CaO: 8.74</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 0.00</th>
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<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;: 20.70</td>
<td>FeO: 21.77</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
<td>ZnO: 0.00</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;: 0.00</td>
<td>MnO: 11.50</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;O: 0.00</td>
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</table>
### ROCK NO. 86-10 MUSCOVITE ANAL NO. 8

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>47.12 Mo: 2.00 Ca: 0.00 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.68 FeO: 3.63 Na₂O: 0.56 BaO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.35 MnO: 0.02 K₂O: 10.25 Total: 93.61</td>
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</table>

**MINERAL FORMULA NO. OF OXYGENS = 11.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(MUSC) = 0.53661336
- A(CELAD) = 0.10087049
- A(MARG) = 0.0000000000

### ROCK NO. 86-10 MUSCOVITE ANAL NO. 9 MUS 2

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.04 Mo: 1.85 Ca: 0.00 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.70 FeO: 3.63 Na₂O: 0.46 BaO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.40 MnO: 0.01 K₂O: 10.14 Total: 93.23</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 11.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(MUSC) = 0.539741665
- A(CELAD) = 0.093395707
- A(MARG) = 0.0000000000

### ROCK NO. 86-10 MUSCOVITE ANAL NO. 10

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.29 Mo: 2.06 Ca: 0.00 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.57 FeO: 3.61 Na₂O: 0.55 BaO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.32 MnO: 0.01 K₂O: 10.20 Total: 93.61</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 11.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(MUSC) = 0.5303500295
- A(CELAD) = 0.1041282415
- A(MARG) = 0.0000000000

### ROCK NO. 86-10 BIOTITE ANAL NO. 12

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.86 Mo: 8.92 Ca: 0.01 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.51 FeO: 21.49 Na₂O: 0.11 F: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.12 MnO: 0.20 K₂O: 9.40 Total: 94.92</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 9.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(OH-PHLOG) = 0.0365713611
- A(OH-ANN) = 0.0966285183

---

### ROCK NO. 84-1 GARNET ANAL NO. 8 NR. AM.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.01 Mo: 1.54 Ca: 0.05 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.15 FeO: 28.15 Na₂O: 0.00 ZrO₂: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.06 MnO: 2.47 K₂O: 0.00 Total: 100.20</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 12.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(CLINGO) = 0.0121401684

### ROCK NO. 86-10 CHLORITE ANAL NO. 13

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>27.16 Mo: 12.58 Ca: 0.03 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.68 FeO: 27.20 Na₂O: 0.10 NiO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.00 MnO: 0.34 K₂O: 0.10 Total: 88.30</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 14.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(CLINGO) = 0.0133581414

### ROCK NO. 86-10 CHLORITE ANAL NO. 15

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>27.16 Mo: 12.58 Ca: 0.03 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.68 FeO: 27.20 Na₂O: 0.10 NiO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.00 MnO: 0.34 K₂O: 0.10 Total: 87.28</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 14.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(CLINGO) = 0.0133581414

---

### ROCK NO. 86-10 CHLORITE ANAL NO. 16

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight-% Oxides (FeO = Fe-TOTAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>24.33 Mo: 11.78 Ca: 0.03 Cr₂O₃: 0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.61 FeO: 28.27 Na₂O: 0.00 NiO: 0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.10 MnO: 0.34 K₂O: 0.00 Total: 85.45</td>
</tr>
</tbody>
</table>

**MINERAL FORMULA NO. OF OXYGENS = 14.**

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL):**

- A(CLINGO) = 0.0110059410
ROCK NO - 86-8  MUSCOVITE  ANAL NO- 20
WEIGHT-% OXIDES ( FeO = Fe-TOTAL )

SiO₂: 46.76  MgO: 1.93  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 29.25  FeO: 2.67  Na₂O: 0.39  BA(OH): 0.00
TiO₂: 0.18  MnO: 0.00  K₂O: 10.00  Total: 94.38

MINERAL FORMULA NO. OF OXYGENS = 11.

Si: 3.262  Mg: 0.201  Ca: 0.000  Cr: 0.000
Al: 2.468  Fe₂: 0.156  Na: 0.053  Ba: 0.000
Ti: 0.020  Mn: 0.000  K: 0.840  Fe₃: 0.000

THERMODYNAMIC ACTIVITIES ( ON-SITES MIXING MODEL )
A(MUSC) = 0.5811294758  A(CELAD) = 0.1103909019
A(PARAG) = 0.0332604088  A(MARG) = 0.0000000000

ROCK NO - 86-8  MUSCOVITE  ANAL NO- 21
WEIGHT-% OXIDES ( FeO = Fe-TOTAL )

SiO₂: 47.58  MgO: 1.93  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 30.03  FeO: 3.34  Na₂O: 0.50  BA(OH): 0.00
TiO₂: 0.00  MnO: 0.000  K₂O: 10.00  Total: 94.38

MINERAL FORMULA NO. OF OXYGENS = 11.

Si: 3.255  Mg: 0.197  Ca: 0.000  Cr: 0.000
Al: 2.127  Fe₂: 0.191  Na: 0.066  Ba: 0.000
Ti: 0.000  Mn: 0.000  K: 0.873  Fe₃: 0.000

THERMODYNAMIC ACTIVITIES ( ON-SITES MIXING MODEL )
A(MUSC) = 0.5493933470  A(CELAD) = 0.0984022222
A(PARAG) = 0.0414864042  A(MARG) = 0.0000000000

ROCK NO - 86-8  MUSCOVITE  ANAL NO- 23
WEIGHT-% OXIDES ( FeO = Fe-TOTAL )

SiO₂: 49.56  MgO: 2.34  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 28.98  FeO: 3.55  Na₂O: 0.46  BA(OH): 0.00
TiO₂: 0.36  MnO: 0.000  K₂O: 4.92  Total: 95.17

MINERAL FORMULA NO. OF OXYGENS = 11.

Si: 3.231  Mg: 0.234  Ca: 0.000  Cr: 0.000
Al: 2.290  Fe₂: 0.199  Na: 0.066  Ba: 0.000
Ti: 0.018  Mn: 0.000  K: 0.848  Fe₃: 0.000

THERMODYNAMIC ACTIVITIES ( ON-SITES MIXING MODEL )
A(MUSC) = 0.4753924222  A(CELAD) = 0.1220785379
A(PARAG) = 0.0335038640  A(MARG) = 0.0000000000

ROCK NO - 86-8  MUSCOVITE  ANAL NO- 24
WEIGHT-% OXIDES ( FeO = Fe-TOTAL )

SiO₂: 48.28  MgO: 1.70  CaO: 0.00  Cr₂O₃: 0.00
Al₂O₃: 31.26  FeO: 2.45  Na₂O: 0.64  BA(OH): 0.00
TiO₂: 0.38  MnO: 0.000  K₂O: 9.84  Total: 94.81

MINERAL FORMULA NO. OF OXYGENS = 11.

Si: 3.239  Mg: 0.170  Ca: 0.000  Cr: 0.000
Al: 2.473  Fe₂: 0.137  Na: 0.090  Ba: 0.000
Ti: 0.019  Mn: 0.001  K: 0.842  Fe₃: 0.000

THERMODYNAMIC ACTIVITIES ( ON-SITES MIXING MODEL )
A(MUSC) = 0.5677644876  A(CELAD) = 0.0839040999
A(PARAG) = 0.0605045454  A(MARG) = 0.0000000000
### ROCK NO. 86-8 GARNET ANAL NO. 28

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.41</td>
<td>1.40</td>
<td>9.18</td>
<td>0.00</td>
<td>87.07</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 32

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(CLINOCL) = 0.0103190131

---

### ROCK NO. 86-8 GARNET ANAL NO. 28

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.30</td>
<td>0.73</td>
<td>8.70</td>
<td>0.00</td>
<td>87.73</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 32

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(CLINOCL) = 0.0103401503

---

### ROCK NO. 86-8 GARNET ANAL NO. 29

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.97</td>
<td>1.15</td>
<td>9.19</td>
<td>0.00</td>
<td>87.31</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 32

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(CLINOCL) = 0.0072074817

---

### ROCK NO. 86-8 CHLORITE ANAL NO. 29

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.42</td>
<td>0.48</td>
<td>0.00</td>
<td>0.00</td>
<td>84.90</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 14

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(CLINOCL) = 0.006/132346

---

### ROCK NO. 86-8 CHLORITE ANAL NO. 30

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.86</td>
<td>1.15</td>
<td>9.19</td>
<td>0.00</td>
<td>87.30</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 14

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(CLINOCL) = 0.0384026865

---

### ROCK NO. 86-8 MUSCOVITE ANAL NO. 30

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.52</td>
<td>0.43</td>
<td>0.00</td>
<td>0.00</td>
<td>83.45</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**WEIGHT-% OXIDES**  
(Fe₂O₃ = Fe-TOTAL)

**MINERAL FORMULA**  
NO. OF OXYGENS = 14

**THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL)**

A(MUSC) = 0.06/41978812
A(CELAD) = 0.0384026865
A(PARAG) = 0.1269761324
A(MARG) = 0.0000000000
<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>MUSCOVITE</th>
<th>ANAL NO.: 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 47.00 MgO: 0.08 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 35.25 Fe₂O₃: 1.16 Na₂O: 1.33 BaO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.30 MnO: 0.00 K₂O: 0.04 Total: 94.76</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 11. |
| Si : 3.125 Mg : 0.008 Ca : 0.000 Cr : 0.000 |
| Al : 2.763 Fe₂: 0.094 Na : 0.171 Ba : 0.000 |
| Ti : 0.015 Mn : 0.000 K : 0.767 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(MUSC) = 0.6698618652 |
| A(CELAD) = 0.0034725515 |
| A(PARAG) = 0.1497712731 |
| A(MARG) = 0.0000000000 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>MUSCOVITE</th>
<th>ANAL NO.: 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 44.60 MgO: 1.49 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 35.00 Fe₂O₃: 4.40 Na₂O: 1.16 BaO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.24 MnO: 0.00 K₂O: 8.50 Total: 95.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 11. |
| Si : 2.993 Mg : 0.149 Ca : 0.000 Cr : 0.000 |
| Al : 2.764 Fe₂: 0.247 Na : 0.151 Ba : 0.000 |
| Ti : 0.012 Mn : 0.000 K : 0.728 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(MUSC) = 0.4686670575 |
| A(CELAD) = 0.0282962828 |
| A(PARAG) = 0.0972122350 |
| A(MARG) = 0.0000000000 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>MUSCOVITE</th>
<th>ANAL NO.: 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 46.23 MgO: 0.87 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 35.51 Fe₂O₃: 1.21 Na₂O: 0.85 BaO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.26 MnO: 0.00 K₂O: 9.87 Total: 94.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 11. |
| Si : 3.086 Mg : 0.067 Ca : 0.000 Cr : 0.000 |
| Al : 2.795 Fe₂: 0.068 Na : 0.110 Ba : 0.000 |
| Ti : 0.013 Mn : 0.000 K : 0.841 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(MUSC) = 0.7187030911 |
| A(CELAD) = 0.0253693419 |
| A(PARAG) = 0.0946669779 |
| A(MARG) = 0.0000000000 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>MUSCOVITE</th>
<th>ANAL NO.: 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 45.54 MgO: 10.48 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 22.63 Fe₂O₃: 30.32 Na₂O: 0.00 NiO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.24 MnO: 0.00 K₂O: 0.00 Total: 94.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 14. |
| Si : 2.563 Mg : 1.701 Ca : 0.000 Cr : 0.000 |
| Al : 2.905 Fe₂: 2.761 Na : 0.000 Ni : 0.000 |
| Ti : 0.014 Mn : 0.023 K : 0.000 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(CLILO) = 0.0056977198 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>CHLORITE</th>
<th>ANAL NO.: 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 23.20 MgO: 10.57 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 22.43 Fe₂O₃: 30.16 Na₂O: 0.00 NiO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.09 MnO: 0.27 K₂O: 0.00 Total: 96.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 14. |
| Si : 2.550 Mg : 1.732 Ca : 0.000 Cr : 0.000 |
| Al : 2.907 Fe₂: 2.773 Na : 0.000 Ni : 0.000 |
| Ti : 0.005 Mn : 0.025 K : 0.000 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(CLILO) = 0.0061755367 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>CHLORITE</th>
<th>ANAL NO.: 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂: 23.20 MgO: 10.57 CaO: 0.00 Cr₂O₃: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃: 22.43 Fe₂O₃: 30.16 Na₂O: 0.00 NiO: 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂: 0.09 MnO: 0.27 K₂O: 0.00 Total: 96.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MINERAL FORMULA NO. OF OXGENS = 14. |
| Si : 2.550 Mg : 1.735 Ca : 0.000 Cr : 0.000 |
| Al : 2.907 Fe₂: 2.773 Na : 0.000 Ni : 0.000 |
| Ti : 0.005 Mn : 0.025 K : 0.000 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(CLILO) = 0.0061796065 |

<table>
<thead>
<tr>
<th>ROCK NO.: 71-3</th>
<th>CHLORITE</th>
<th>ANAL NO.: 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT-% OXIDES (FeO = Fe-TOTAL)</td>
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<tr>
<td>SiO₂: 23.39 MgO: 10.68 CaO: 0.00 Cr₂O₃: 0.00</td>
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<tr>
<td>Al₂O₃: 22.54 Fe₂O₃: 29.84 Na₂O: 0.00 NiO: 0.00</td>
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<td></td>
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<tr>
<td>TiO₂: 0.04 MnO: 0.27 K₂O: 0.00 Total: 89.81</td>
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</table>

| MINERAL FORMULA NO. OF OXGENS = 14. |
| Si : 2.561 Mg : 1.743 Ca : 0.000 Cr : 0.000 |
| Al : 2.906 Fe₂: 2.732 Na : 0.000 Ni : 0.000 |
| Ti : 0.007 Mn : 0.025 K : 0.000 Fe₃ : 0.000 |

| THERMODYNAMIC ACTIVITIES (ON-SITES MIXING MODEL) |
| A(CLILO) = 0.0084412467 |
The depositional age of the Dalradian Supergroup: U-Pb and Sm-Nd isotopic studies of the Tayvallich Volcanics, Scotland.

by

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ABSTRACT
Zircons from a keratophyre associated with the Tayvallich Volcanics in the Dalradian rocks of the SW Scottish Highlands have been dated by U-Pb methods, yielding an age of 595 ± 4 Ma. This age indicates that most or all of the Dalradian is Precambrian in age, and that Dalradian sedimentation may have lasted for about 200 million years. The age also constrains the time interval between cessation of Dalradian sedimentation and subsequent crustal thickening and regional metamorphism during the Grampian Orogeny. Sm-Nd isotopic data for the Tayvallich Volcanics and related metadolerite sills yield initial εNd values of +2 to +4, which are thought to reflect the effects of melting of lithospheric mantle.
The Dalradian Supergroup in the metamorphic Caledonides of Scotland and Ireland has traditionally been considered to comprise a very thick sequence of late Precambrian to Cambrian age, evolving from shales, sandstones and limestones upwards into greywackes and volcanics (Harris and Pitcher, 1975). The oldest Appin Group rocks in the SW Highlands (Fig. 1) were deposited in a shelf environment, and the subsequent Argyll Group rocks were deposited in a series of subsiding, fault-bounded sedimentary basins, showing evidence of increasing tectonic instability of a subsiding continental margin (Anderton 1982, 1985). The lowermost rocks of the Southern Highland Group indicate the onset of basaltic volcanism in the SW Highlands, represented by the Tayvallich Volcanics and the related sill complex (Graham, 1976), giving way upwards to greywackes and further volcanics.

Various tectonic settings have been proposed for the development of the Dalradian basins, including ensialic basins (Harris et al. 1978), a transtensional tectonic setting (Graham and Borradaile, 1984; Graham, 1986), and the northwestern margin of an evolving Lower Palaeozoic Iapetus Ocean (Anderton 1982, 1985; Graham and Bradbury, 1981). Tectonic reconstructions or modern day comparisons require a knowledge of the timing of the relevant events. The uncertainty surrounding the depositional ages of the Dalradian and Moinian successions and their along-strike equivalents is a major obstacle of an understanding of the late Proterozoic and Lower Palaeozoic evolution of the North Atlantic region.

**Previous age estimates for the Dalradian**

(1) The Dalradian is younger than the late Proterozoic Moine metasediments which make up the bulk of the Scottish Highlands. The latter are in turn older than the cross-cutting Ardgour Granite Gneiss (Rb-Sr age 1030 ± 50 Ma, Brook et al. 1976). Pegmatites associated with the slide separating the Moine (Central Highland Division) from Grampian Group Dalradian rocks (which underlie the Appin Group
Dalradian in the Central Highlands) yield Rb-Sr ages of up to 780 Ma (Piasecki and van Breemen, 1979; van Breemen et al. 1978), and were thought by Soper and Anderton (1984) to be the result of lithospheric stretching and thinning during the initial formation of the Dalradian basin.

(2) The Portaskaig Tillite at the base of the Argyll Group is almost certainly equivalent in age to the Varanger Tillites of Scandinavia, from which a meta-pelite has yielded a Rb-Sr apparent age of 668 ± 23 Ma (Pringle, 1973). There appears to be no way of assessing whether this "age" truly dates sedimentation or whether it is affected by relic detrital components and/or metamorphism.

(3) The Dalradian is cut by the Ben Vuirich granite which is dated by U-Pb analyses of zircons defining a lower intercept with concordia of 514 ±6 Ma (Pidgeon and Aftalion, 1978). Lower intercept U-Pb ages using bulk zircon separates are in need of verification using more modern single-grain methods.

(4) Downie et al. (1971) have tentatively assigned a Lower Cambrian age to the uppermost Argyll Group (Tayvallich Limestone) which directly underlies the Tayvallich Volcanics on the basis of acritarchs which have comparable characteristics to those of the Lower Cambrian Bellaskaja Series of Siberia, and have suggested that the base of the Cambrian may be below the Tayvallich Limestone and above the Easdale Slate. The Leny Limestone at Callander, adjacent to the Highland Border, was assigned a Lower Cambrian age (Pringle, 1939) based on undoubted Lower Cambrian trilobites and brachiopods. The relationship of this limestone to the Southern Highland Group to the north and to the Highland Border Complex rocks (of Ordovician age; Curry et al. 1984) to the south has remained uncertain.

Basaltic volcanics in the Dalradian

Pre-tectonic mafic igneous rocks are abundant within the Dalradian Supergroup in some parts of the British and Irish Caledonides, most particularly in the SW Scottish Highlands where a thick metadolerite-metagabbro sill complex and overlying submarine pillow lavas, pillow breccias and hyaloclastites (the Tayvallich
Volcanics) form a cumulative exposed thickness of over 5km (about 30% of the exposed Dalradian succession) (Graham, 1976; Graham and Bradbury, 1981). Northeastwards across the trans-Caledonoid Cruachan Lineament the proportion of these mafic rocks within the Dalradian succession is greatly reduced (Graham, 1986). Thick feeder dykes to the mafic suite intrude the Appin Group in Jura (Graham and Borradaile, 1984). The suite has undergone extensive sub-seafloor spilitic alteration, but mafic rocks unaffected by spilitic alteration have a tholeiitic, quartz- or hypersthene-normative major element chemistry. Incompatible trace element characteristics are intermediate between those typical of continental basalts and those of MORB (Graham 1976, Graham and Bradbury 1981, Graham and Borradaile 1984).

The tectonic setting of Dalradian mafic igneous rocks has been variously interpreted. In the light of the petrochemistry and field relations of these rocks, Graham (1976) and Graham and Bradbury (1981) ascribed them to a rifting environment associated with crustal separation, formation of "embryonic" ocean crust and opening of the Iapetus Ocean, or some marginal basin to the NW of an already-existing Iapetus Ocean, in late Precambrian or Lower Cambrian time. This model was thought to be compatible with the sedimentary evidence compiled by Anderton (1982, 1985), who also argued that Iapetus did not open till the Cambrian. Recent models (Graham & Borradaile, 1984; Fettes et al. 1986; Graham, 1986) suggest an alternative and very different transcurrent or transtensional tectonic setting in which Dalradian mafic igneous rocks are viewed as a key element in a quasi-oceanic trans-Caledonoid pull-apart basin in the SW Scottish Highlands, bounded to the NE by the Cruachan Lineament. Pre-Grampian Dalradian evolution in this alternative model occurred to the NW of a dextral transcurrent plate margin, possibly in the vicinity of (but not along) the present-day Highland Boundary fault, and therefore Dalradian volcanism and sedimentation provide no evidence relevant to the development or existence of an Iapetus Ocean to the SE in late Precambrian-early Cambrian time.
The style of igneous activity, dominated by sill intrusion into a thick sedimentary pile, and the implied transcurrent tectonic setting, both suggest analogy with the evolution of the present-day Gulf of California (Anderton, 1985; Graham & Borradaile, 1984; Graham, 1986).

**U-Pb and Sm-Nd Isotopic Studies**

Rare Zr-rich quartz-keratophyres and feldspar porphyries occur as subvolcanic intrusive bodies associated with the Tayvallich Volcanics in the Tayvallich Peninsula (Fig. 1) (Peach et al. 1911, Graham 1976, Gower 1977). These rocks are geochemically related to the overlying Tayvallich Volcanics and underlying metadolerite sill complex by fractionation schemes and processes discussed in detail by Graham (1976). The keratophyre sampled for this geochronological study is a pinkish-grey feldspar porphyry rock from a small laccolithic body from the west coast of the Tayvallich Peninsula ([NR 695822]; see Gower (1977) for field relations). Large lithologically-similar blocks occur as clasts in overlying volcanic breccias, supporting geochemical evidence that the keratophyre is cogenetic with the basic volcanics.

The mineralogy and chemistry of the sampled keratophyre are described by Peach et al. (1911), and indicate a very high sodium and low potassium content. Large tabular albitic feldspar 'megacrysts' up to 3mm in length, many showing chessboard twinning, occur in a finer 'trachytic'-textured albite-rich matrix containing in addition quartz, epidote, white mica, chlorite and opaques. Although the rock now has a low-grade metamorphic mineral assemblage, compatible with the greenschist facies metamorphism of the adjacent metabasic and metasedimentary rocks, there is no evidence of a deformation fabric in the samples studied.

U-Pb data are presented in Table 1 for four slightly magnetic size fractions of zircons from this keratophyre. Analytical techniques are presented elsewhere (Krogh, 1973; Pidgeon and Aftalion, 1978; Halliday et al. 1984a). The zircon population consists mainly of euhedral, squat, very fragmented, yellowish, clear
crystals. Some black and some clear inclusions, outgrowth, overgrowth and some parallel growth are common, together with cracks and embayments. Occasionally some iron staining can be seen. The four size fractions and two repeats yield discordant U-Pb ages which, when plotted on a concordia diagram, define a linear array which intersects concordia at 597 Ma and the present day but with a large extrapolated maximum intercept age uncertainty. This is to some extent an artefact of the fact that the discordia line intersects concordia at a shallow angle. Dunning and Krogh (1985) have suggested that this intercept problem can be handled by fixing the lower intercept at zero age. This gives the same solution to that of a simple least-squares fit to the data, ie. an intercept age of 597 Ma. If Pb-loss has taken place only recently, the $^{207}\text{Pb}/^{206}\text{Pb}$ ages should be uniform and define the original crystallization age. Examination of the data in Table I shows that there is in fact a slight spread from 590 to 603, the mean being $595 \pm 4$ Ma. This is taken as the best estimate of the age of the keratophyre, although we note that the other ages from the zircons with least lead loss would define an age of $598 \pm 5$ Ma which is only marginally different.

Sm-Nd isotopic and concentration data for four samples of basic Tayvallich Volcanics and metadolerite, and two samples of cogenetic keratophyre are presented in Table 2. Techniques are described elsewhere (Halliday et al. 1984b; Hamilton et al. 1984). The Sm/Nd ratios are typical of LREE-enriched rocks and endorse the evidence already discussed that the basalts are formed from well-fractionated magmas. $\epsilon$Nd values have been calculated for 597 Ma, the apparent age of the volcanics. These range from +2 to +4, notably lower than present-day MORB compositions which range down to approximately +8.

Discussion

The U-Pb age and initial $\epsilon$Nd values for the Tayvallich Volcanics place some important new constraints on the age and evolution of the Dalradian, and on the evolution of this section of the Caledonides.
1. The Dalradian is largely Precambrian in age, being older than 590 Ma, which is the oldest recent estimate of the age of the Precambrian/Cambrian boundary (Harland et al. 1982), also put by some at 530 Ma (Odin et al. 1982) and by others at 570 Ma (Palmer 1983). In addition, supposed Lower Cambrian acritarchs of the Argyll Group (Downie et al. 1971) must also be Precambrian.

2. In the light of the c. 600 Ma age of the Tayvallich Volcanics, the trilobite-bearing Leny Limestone could still belong to the Southern Highland Group, consistent with a Lower Cambrian upper age limit for Dalradian sedimentation.

3. If the model of Soper and Anderton (1984) is correct, and the 780 Ma ages for Morarian pegmatites date the opening of the Dalradian sedimentary basin, then Dalradian sedimentation lasted for about 200 million years.

4. The initial εNd values are consistent with the hypothesis that the Tayvallich Volcanics are not normal MORB-type material. We suggest that they were derived from melting of sub-continental mantle lithosphere in a transtensional environment.

5. The age of the Tayvallich Volcanics constrains the time interval between cessation of Dalradian sedimentation and subsequent crustal thickening and regional metamorphism during the Grampian Orogeny, given that in any reasonable conductive thermal model of Dalradian metamorphism (eg. Dempster 1985) crustal thickening must precede the attainment of peak metamorphic conditions by a time interval of 20-40 million years, depending upon the magnitudes of the controlling thermal parameters (England & Richardson, 1977).

6. The Tayvallich Limestone, which underlies the Tayvallich Volcanics, is the uppermost lithostratigraphic unit of the Argyll Group and is correlated with the Loch Tay Limestone (Harris & Pitcher, 1975), a distinctive marker horizon throughout the Dalradian. These are the youngest widely-occurring carbonates in the Dalradian. Our radiometric data demonstrate conclusively that these limestones are Precambrian in age, and are therefore substantially older than the carbonates of the Cambro-Ordovician succession unconformably overlying Lewisian and Torridonian rocks of
the Caledonian foreland of the northwest Scottish Highlands. The Cambro-
Ordovician shelf of the northwest Highland Caledonian foreland need not therefore
have constituted a physical barrier to any northwesterly provenance for Dalradian
clastic sediments.

7. A global rifting event at the Precambrian/Cambrian boundary (circa 600 Ma
in the N Atlantic region) seems well established (Bond et al. 1984) and the Tayvallich
Volcanics correspond in age with this event. Certain minor intrusives into supposed
Lewisian and Torridonian rocks on Colonsay (Fig. 1) have also been dated at 'about
600 Ma' by Ar/Ar analysis of hornblende (Bentley et al. 1988). In the case of the
Dalradian the rifting event merely affected a pre-existing basin which had already
been actively evolving for 200 million years. The depositional history and early
evolution of the Dalradian cannot therefore be explained simply as the result of this
rifting event. The precise tectonic relationship between this global rifting event and
Dalradian basaltic igneous activity at c. 600 Ma remains obscure (Graham, 1986).
Acknowledgements

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REFERENCES


CMG\PRE-CAM.DOC (B)
Table 1: Zircon-U-Pb-isotopic data, keratophyre, Tayvallich

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<tr>
<th>Size Fractions (nm)</th>
<th>Pb (ppm)</th>
<th>U (ppm)</th>
<th>206 Pb/204 Pb</th>
<th>206 Pb</th>
<th>207 Pb</th>
<th>208 Pb</th>
<th>Atom percent radiogenic Pb</th>
<th>Atomic ratios</th>
<th>Apparent ages (Ma)</th>
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<tr>
<td>+106 NW50</td>
<td>19.9</td>
<td>194</td>
<td>2207</td>
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<td>4.6951</td>
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<td>598</td>
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The Pb isotopic concentrations are corrected for common lead, using the Pb- composition of the HNO3 which is thought of as the main contaminant. The assumed 1σ - errors for the isotopic ratios are \( \frac{207 \text{Pb}}{206 \text{Pb}} = 0.1\% \), \( \frac{207 \text{Pb}}{235 \text{U}} = 0.3\% \), \( \frac{206 \text{Pb}}{238 \text{U}} = 0.2\% \) a correlation factor of 0.8 is used for the modified York-concordia intercept computing. For the calculation of the ages the decay constants from Jaffey et al. 1971 are used with \( \lambda_{235 \text{U}} = 0.98485 \times 10^{-9} \text{ yrs}^{-1} \) and \( \lambda_{238 \text{U}} = 0.155125 \times 10^{-9} \text{ yrs}^{-1} \).
Table 2: Sm-Nd isotopic data for Tayvallich volcanics

<table>
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<tr>
<th>Sample Number</th>
<th>Lithology</th>
<th>Sm (ppm)</th>
<th>Nd (ppm)</th>
<th>$^{147}<em>{\text{Sm}}/^{144}</em>{\text{Nd}}$ *</th>
<th>$^{143}<em>{\text{Nd}}/^{144}</em>{\text{Nd}}$ *</th>
<th>$^{143}<em>{\text{Nd}}/^{144}</em>{\text{Nd}}$ ± 2σm</th>
<th>εt Nd</th>
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<tbody>
<tr>
<td>84-49</td>
<td>keratophyre</td>
<td>24.25</td>
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<td>.11383</td>
<td>.512484±16</td>
<td>.51204</td>
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<td>69-296</td>
<td>metabasalt</td>
<td>8.463</td>
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<td>.512564±15</td>
<td>.51208</td>
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<td>5.115</td>
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<td>.17021</td>
<td>.512648±14</td>
<td>.51198</td>
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* Uncertainty in $^{147}_{\text{Sm}}/^{144}_{\text{Nd}}$ estimated at less than 0.3%.

Errors quoted for $^{143}_{\text{Nd}}/^{144}_{\text{Nd}}$ refer to last significant digits and are run precisions (2σ mean).

$t = 597$ Ma

$\lambda = 6.54 \times 10^{-12}$ yr$^{-1}$

Present day bulk earth parameters are $^{147}_{\text{Sm}}/^{144}_{\text{Nd}} = 0.1966$, $^{143}_{\text{Nd}}/^{144}_{\text{Nd}} = 0.512538$.
FIGURE CAPTIONS

Fig. 1 Map of Scottish Highlands showing outcrop of major divisions of Dalradian and Moine rocks, and location of Tayvallich.

Fig. 2 Concordia diagram of U-Pb zircon data for the keratophyre from the Tayvallich Volcanics.
$^{206}\text{Pb} / ^{238}\text{U}$

$^{207}\text{Pb} / ^{235}\text{U}$

600 Ma

550 Ma

$^{2\sigma}$ error box