

THESIS, SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF OXFORD

METAMORPHIC STUDIES IN THE SCOTTISH HIGHLANDS

by

ANDREW JAMES BAKER

of LINACRE COLLEGE

and the DEPARTMENT OF EARTH SCIENCES,

UNIVERSITY OF OXFORD

VOLUME 1 TEXT



SHORT ABSTRACT

Metamorphic Studies in the Scottish Highlands, DPhil thesis by A. J. Baker of Linacre College (Hilary Term, 1985).

Conditions of 8kb and 800°C are estimated for sillimanite K feldspar bearing metapelites and garnet-clinopyroxene bearing amphibolites in Glen Muick. These conditions are inconsistent with the simultaneous nearby presence of equilibrium between andalusite and kyanite. Andalusite in the Glen Muick area is late. The sillimanite zone may have been in part primary. There is a transition without major structural break between Tay Nappe flat belt and the "Banff Nappe".

A dataset has been derived for phases in the system KCMASHCO₂. The MHSRK equation of Kerrick and Jacobs (1981) has been used to extract data from mixed devolatilisation equilibria. Heats of formation are in agreement with calorimetrically determined values. Phlogopite equilibria calculated using disordered phlogopite data seem most appropriate to natural metapelite assemblages.

Variations in pressure and temperature have been constrained across the Dalradian using various calibrated reactions. Temperatures vary from about 500°C in the low kyanite zone to 800°C in the sillimanite-K feldspar zone and pressures vary from 4kb to 10kb. Pressure estimates are justified on the basis that they are consistent with the aluminosilicate phase diagram. Rocks from the Central Highlands to Glen Clova underwent a decrease in pressure during evolution through peak metamorphic conditions. Amphibolites from the southern Moines show evidence of a former eclogitic assemblage of early Grampian age or earlier.

High temperature regional metamorphic rocks lie at high structural levels and are suggested to be an allochthonous unit, the Banff Nappe of Grampian age. The western margin of the Banff Nappe is marked by a temperature maximum to the immediate east, sharp thermal transitions, a train of metabasites and a high strain zone. It is suggested that emplacement of a Banff Nappe resulted in the deformation and metamorphism of structurally lower rocks.

LONG ABSTRACT

Conditions of 8kb at 800°C have been estimated for sillimanite-K feldspar bearing metapelites and garnet clinopyroxene bearing metabasites in Glen Muick. A garnet clinopyroxene zone may be distinguished in metabasites within the sillimanite zone. These conditions are in excess of those previously envisaged for this part of the Dalradian. Previous workers have inferred that metamorphism in the Glen Muick area occurred at pressures below the aluminosilicate polymorph triple point. However, andalusite in the Glen Muick area is late and was not synchronous with the peak metamorphic conditions. It is, in part, of contact metamorphic origin and may also result from regional retrogression.

There is a gradual transition from the sillimanite zone, to the south of Glen Muick, to the sillimanite K feldspar zone in Glen Muick. To the west however, there is a very rapid transition to lower grade AFM kyanite-staurolite-biotite zone rocks. This abrupt transition coincides with a band of serpentinite and metagabbro. Extensive retrogression occurs in the Glen Muick-Cromar areas. It is uncertain whether this is entirely attributable to the abundant Newer Granites in the area.

There is an apparent transition, without apparent major structural break, between the Tay Nappe flat belt and the Banff Nappe through the Glen Muick area. The Cromar Deeside Gneisses are similar, stratigraphically and metamorphically, to the Duchray Hill Gneiss further to the southeast. If the Cromar gneisses comprise a slice of Pre-Cambrian basement then the Duchray Hill Gneiss must also be Pre-Cambrian. This hypothesis does not appear to be acceptable.

The fact that andalusite is late in the Glen Muick area shows that it cannot have been in equilibrium with kyanite, which is considered to be an early phase in this area. The sequence of polymorph development kyanite → sillimanite → regional (?) andalusite is found in the Glen Muick area.

The former presence of a kyanite andalusite isograd through the Glen Muick area is rejected on the basis of this late andalusite. The andalusite-kyanite isograd may lie to the north of this area in Donside. Alternatively it may never have existed within the sillimanite zone. During a progressive metamorphic event P-T evolution would cause equilibrium between andalusite and kyanite to occur in different places at different times. No one position of the isograd would be valid. A "primary" sillimanite zone may have existed synchronous with other zones to the north and the south. The sillimanite "overprint" does not necessarily mean that sillimanite was significantly later than other peak thermal events outside the sillimanite zone. Sillimanite in Glen Muick is synchronous with the last major phase of deformation. Sillimanite to the south postdates the last major phase of deformation.

Most of the area studied lies within the aluminosilicate zones. Garnet chlorite assemblages however appear to be stable in the Ailnack Gorge area. In Glen Avon there is apparent equilibrium between garnet and chlorite in some muscovite+quartz bearing rocks, but generally it seems to be retrogressive. Paragonite-quartz is stable in Glen Avon and to the west of the Duchray Hill Gneiss and margarite-quartz in Glen Ey. In Glen Avon, the Ailnack Gorge and along the Banff Coast, west of Portsoy the assemblages muscovite-zoisite-calcite-quartz and rutile-calcite-quartz are stable. Staurolite-biotite Fe-Mg exchange appears to be temperature sensitive. It may be of limited use as a crude thermometrical indicator. Metabasites from the Central Highlands to Glen Clova contain variably resorbed garnets which are replaced by plagioclase and sometimes zoisite. This reaction probably represents decreasing pressures.

A dataset has been derived for a subset of phases in the system $KCMASH_2OCO_2$. The experimental data considered includes both

determinations of high pressure phase equilibria and lower pressure mixed volatile equilibria. In particular, the phase pyrope has been added to the dataset, derived by Helgeson et al. (1978). Equilibria of geological interest have been calculated using this dataset. Heats of formation have been derived from the experimental data and are in good agreement with direct calorimetric measurements. A number of reactions involving phlogopite have been calculated. Assuming that natural biotites are tetrahedrally disordered and using the experimental data of Wones and Dodge (1966) for disordered phlogopite gives reasonable results, while using data for ordered phlogopite does not.

Reactions useful as geothermobarometers, calibrated in the literature and those derived from the thermodynamic analysis of chapter 5, have been used to constrain pressure and temperature across the Dalradian. Other reactions have been used to constrain fluid compositions. The barometers employed produce results which are mutually consistent and which agree with the aluminosilicate phase diagram. The sense of temperature variation deduced from garnet biotite exchange thermometry, staurolite-biotite Fe-Mg exchange and biotite M/FM data in the assemblage kyanite-staurolite-biotite is the same. Garnet-amphibole and garnet clinopyroxene exchange thermometers, data on the aluminosilicate phase diagram and the stability of various assemblages (muscovite-calcite-quartz, muscovite-zoisite-quartz, rutile-calcite-quartz, paragonite-quartz and margarite-quartz) are also consistent with the above estimates.

Temperatures vary from 550°C in the low kyanite zone to about 800°C in the sillimanite-K feldspar zone. Pressures vary from just above those appropriate to the aluminosilicate polymorph triple point in Glen Esk to about 10kb in the Central Highlands.

Estimates of $x_{\text{H}_2\text{O}}$ in the fluid suggest that it was very low in the lower part of the kyanite zone. The low values of $X_{\text{H}_2\text{O}}$, if correct, imply

some sort of infiltration for low kyanite zone rocks. Compositions of fluids in equilibrium with graphite were not buffered to maximum water contents. Staurolite equilibria do not appear to read lower than other dehydration reactions, such as paragonite dehydration, as far as this study is concerned.

Evidence for pressure temperature evolution from aluminosilicate polymorph phase relationships, garnet zoning and reactions in metabasites suggests that areas from Glen Clova to the Central Highlands experienced a decrease in pressure during evolution through peak metamorphic temperature. Evidence used to constrain this evolution comprises:

- (1) aluminosilicate polymorph relationships;
- (2) replacement of rutile by ilmenite;
- (3) zoning of adjacent plagioclase and garnet;
- (4) garnet zoning profiles in various assemblages and
- (5) garnet resorption reactions in metabasites.

There is evidence, from sources in the literature, that some areas underwent a pressure increase at a relatively late stage in the thermal evolution. This is attributed to a further phase of tectonic thickening and increased burial as a result of NW directed sliding.

It is emphasised that the conclusions reached in parts of this thesis are dependent upon the approach adopted towards the correlation of deformational and metamorphic events. It is considered that many "correlated" deformational events in the Dalradian are diachronous or unrelated. Strongly diachronous metamorphism is to be expected and different segments of the crust will experience different P-T paths.

The regional variations in pressure and temperature have been constrained. High temperature regional metamorphic rocks lie at high structural levels in NE Scotland. The distribution of pressure and

temperature, derived in this thesis differs from previous thermochemical and isogradic syntheses. The estimated pressures are about 2kb lower than those previously estimated by Wells and Richardson (1979), using a higher pressure calibration of the reaction ALSIL. A number of differences arise with the syntheses of Chinner (1980) and Harte and Hudson (1979). The higher pressures estimated here for the Glen Muick area are one such difference. Control of the regional distribution of recorded pressure and temperature, solely by the effects of post metamorphic folds is not accepted.

A number of rapid transitions in grade are attributed to tectonic processes, synchronous or later than the metamorphic peak. Higher temperatures in NE Scotland may have been attained as the result of additional heat input to the crust while in the Central and SW Highlands metamorphism occurred by a process of tectonic thickening.

Amphibolites from the southern Moines (Central Highlands Granulites) have been found which contain garnets surrounded by plagioclase coronas and diopsidic clinopyroxene-plagioclase symplectites. These are interpreted as former eclogites, but unfortunately their age cannot be satisfactorily constrained. Other amphibolites from this area contain no clinopyroxene of metamorphic origin, but are very similar, suggesting that they too may be interpreted as retrogressed eclogites. Much of the Central Highlands Granulites Moine experienced eclogite facies conditions during either an early phase of the Grampian Orogeny or during an earlier metamorphic event.

A model has been presented which attempts to integrate thermal and tectonic data into a model for the evolution of the Dalradian. A number of features have been found to coincide with the NW margin of the Banff Nappe of Ramsay and Sturt (1979):

- (1) A temperature maximum is reached just to the east.
- (2) Aureoles of synmetamorphic Newer Gabbros are attenuated against this line and a sharp break in grade appears to occur.
- (3) A train of metabasites occurs of debatable significance.
- (4) Zones of intense deformation occur.

The Banff Nappe is interpreted as an allochthonous slice of grampian crust (c.f. Ramsay and Sturt, 1979).

The array of recorded metamorphic pressures implies considerable post metamorphic differential uplift. This differential uplift resulted in the rotation of the crust, the steepening of previously subhorizontal structures and isograds and controls the present disposition of recorded pressure and temperature. Differential uplift may have been achieved by isostatic bending of the crust or the result of deformation occurring at the deeper structural levels.

It is suggested that emplacement of the Banff Nappe first to the SE and then to the NW resulted in metamorphism of deeper rocks. Later rotation of these structurally lower rocks led to the partial preservation of their lower temperature conditions. This model suggests that high temperature metamorphism in the Buchan area occurred before crustal restacking. It is believed that the emplacement of the Banff Nappe was the cause of metamorphism and deformation in structurally lower rocks.

ACKNOWLEDGEMENTS

I am grateful to all the secretarial and technical staff of the department for their assistance at various times. Dr. N. Charnley is thanked for instruction and help with the use of the microprobe.

Dr. G. Droop, and in the latter part of this study, Dr. S. Harley, provided helpful supervision, assistance and discussion. Helpful conversations and discussions with many others relating to this work are acknowledged. Drs. S. W. Richardson and J. Clayburn introduced me to the clinopyroxene bearing garnet amphibolites from the Moine and provided samples.

This work was carried out during the tenure of a N.E.R.C. research studentship which is gratefully acknowledged. The Glen Muick and Balmoral estates are thanked for permitting access.

CONTENTS

CHAPTER 1	page 1
INTRODUCTION	
1.1 Aims	2
1.2 Regional Geology	3
1.3 The Grampian Orogeny	7
1.4 Structural Models	8
1.5 Metamorphism	9
1.6 Igneous Activity	11
1.7 Geochronological data	12
1.8 Correlation	13
1.9 Correlation of metamorphic events	15
1.10 Thermal and tectonic reference frames	18
1.11 Diachroneity in the Grampian Orogeny	20
CHAPTER 2	21
GENERAL PETROLOGY	
2.1 Mineral assemblages and zones in metapelites	23
2.2 Chemical mineralogy of metapelites	26
2.3 Continuous reactions in metapelites	29
2.4 Mineral assemblages and petrography of amphibolites	30
2.5 Chemical Mineralogy of Amphibolites	33
2.6 Amphibole-plagioclase equilibria	34
2.7 Summary	34

CHAPTER 3

page 36

Geology of the Glen Muick Area

3.1	Stratigraphy	37
3.2	Lithologies	39
3.2.1	Metabasites	39
3.2.2	Metapelites	44
3.2.3	Metasedimentary lithologies in Glen Girnock	47
3.3	Metasomatism	48
3.4	Retrogressive metamorphism	49
3.4.1	Hornfelses	49
3.4.2	Retrogressive metamorphism	50
3.4.3	Staurolite bearing assemblages	51
3.4.4	Andalusite bearing assemblages	52
3.5	Mineral Zones	53
3.6	Variations in pressure and temperature	55
3.7	Structure	56
3.7.1	Structural Correlations	58
3.8	Structural-metamorphic relationships	59
3.8.1	Glen Muick	59
3.8.2	Glen Girnock	61
3.9	Conclusions	62

CHAPTER 4

page 64

ALUMINOSILICATE POLYMORPH RELATIONSHIPS

4.1	Glen Muick	65
4.2	Glen Girnock	69
4.3	Lochnagar Granite aureole	69
4.4	S of Glen Muick	70

4.5	Cromar	page 71
4.6	Andalusite and sillimanite elsewhere	73
4.7	Andalusite-sillimanite relationships-a discussion	75
4.8	Deeside andalusite : contact or regional ?	76
4.9	The andalusite-kyanite isograd	77
4.10	Sillimanite versus deformation	82
4.11	Distribution of aluminosilicate zones	83
4.12	Discussion	84
4.13	Conclusions	85

CHAPTER 5

page 87

THERMODYNAMICS OF KCMASHCO₂ EQUILIBRIA

5.1	Calculation methods	89
5.2	Data sources	90
5.3	Reactions involving dolomite and calcite	91
5.4	Discussion of phase equilibrium data	93
5.5	High pressure phase equilibrium data	97
5.6	Chlorite	99
5.7	Thermodynamic data for the phases	100
5.8	Calculation of some reactions in KCMASH	101
5.9	Summary	104

CHAPTER 6

page 105

THERMODYNAMIC ESTIMATION OF THE CONDITIONS OF METAMORPHISM

6.1	Activity models	106
6.2	Thermometry	110
6.3	Geobarometry	113
6.4	Dehydration reactions	118
6.5	Fluids	121
6.6	Melting reactions	122
6.7	The aluminosilicate phase diagram	122
6.8	Results	124
6.8.1	Temperature	124
6.8.2	Pressure	126
6.8.3	Recent barometrical work	131
6.8.4	Fluid compositions	131
6.9	Conclusions	135

CHAPTER 7

137

REGIONAL VARIATIONS IN PRESSURE AND TEMPERATURE

7.1	Patterns of P-T variation	138
7.2	Discussion of previous work	141
7.3	High thermal and baric gradients	145
7.4	Inverted isograds	147
7.5	Discussion	148
7.6	Tectonothermal models	150
7.7	Conclusions	152

CHAPTER 8 page 154

PRESSURE-TEMPERATURE EVOLUTION

8.1	Aluminosilicate polymorph relationships	155
8.2	Early Chloritoid-biotite	156
8.3	Rutile and ilmenite	156
8.4	Plagioclase-garnet equilibria	157
8.5	Reactions in garnet amphibolites	158
8.6	Quantitative P-T paths	158
8.7	Contact metamorphism	161
8.8	Discussion	167
8.9	Conclusions	168

CHAPTER 9 page 169

EVIDENCE FOR HIGH PRESSURE METAMORPHISM IN THE MOINE

9.1	Petrography of some garnet-cpx amphibolites	171
9.2	Chemical Mineralogy	172
9.3	Reaction model	173
9.4	Extent of eclogitic paragenesis	174
9.5	Age	176
9.6	Conclusions	177

CHAPTER 10 page 178

TECTONOTHERMAL MODELS FOR DALRADIAN EVOLUTION

10.1	The Central Highlands	179
10.2	NE Scotland	179
10.3	The Banff Nappe	181
10.4	Differential Uplift	183

	page
10.5 Relationship of metamorphism to structure	184
10.6 The Portsoy Zone	189
10.7 Diachroneity?	192
10.8 Southwards	194
10.9 Metabasites	194
10.10 Summary	198
10.11 Geochronological evidence	199
10.12 Synthesis	200
10.13 The Grampian Orogeny	204
10.14 Conclusions	207
CHAPTER 11	
CONCLUSIONS	209
REFERENCES	218
APPENDIX A	254
ASSEMBLAGES, PETROGRAPHY AND GRID REFERENCES OF SELECTED ROCKS	
APPENDIX B	275
ANALYTICAL DATA AND ZONING PROFILES	
APPENDIX C	296
THERMODYNAMIC BACKGROUND	
APPENDIX D	303
COMPUTER PROGRAMS	

CHAPTER 1

INTRODUCTION

This study is concerned with metamorphic rocks from the Dalradian and Moine Supergroups of the Scottish Highlands (see figure 1.1). It will concentrate on some relatively high grade rocks from the eastern part of the Dalradian. In the first part of this chapter the aims of this thesis are introduced and previous work on the Dalradian and Moine is outlined. In the second part the operation of thermal and deformational processes in orogenic belts will be discussed.

1.1 AIMS

The general and specific problems to be tackled in this thesis will now be briefly introduced. A number of problems concerning the metamorphic evolution will be addressed.

(1) What were the pressures, temperatures and fluid compositions during peak metamorphism. In particular, is it possible to resolve the inconsistencies between high pressures, calculated by Wells and Richardson (1979) and lower ones, estimated by Harte and Hudson (1979)?

(2) What P-T-t paths did rocks follow?

(3) What are the relationships between structural and thermal evolution?

In general, it is hoped that light will be thrown upon the structural evolution of the Dalradian, and of the Grampian Orogeny as a whole.

In an attempt to elucidate P-T paths amphibolites were examined from a number of localities in the Dalradian and to a lesser extent the Moine. In particular, two reports in the very early literature of garnet-clinopyroxene bearing amphibolites were examined. The first from the Moine contained clinopyroxene-plagioclase symplectites and proved to be a retrogressed eclogite.

The second was a garnet-clinopyroxene mafic granulite from Glen Muick in the Dalradian sillimanite zone. The high pressures appropriate to this rock type proved to be inconsistent with the simultaneous presence of regional andalusite generally believed to be present in the area. A more

intensive study was made of the Glen Muick area. The geology of the area is significant, as it lies in the transition from Tay Nappe to a possible Banff Nappe (see below) and near the transition from Barrovian type to Buchan type metamorphism. Study of the area was undertaken in order to:

- (1) clarify the relationships between Banff and Tay Nappes;
- (2) distinguish between possible P-T paths leading to the growth of sillimanite;
- (3) resolve the inconsistency between the high pressures implied by the mafic granulites and the supposed local regional andalusite and
- (4) examine the structural relationships between very high grade regional metamorphic rocks in Glen Muick and the surrounding areas.

In addition, a wider study has been made of the Dalradian in order to constrain the physical conditions of metamorphism and the evolution of these conditions with time. Particular attention has been paid to the relationships between structure and metamorphism. In the latter part of this thesis a structural model is presented in order to attempt to explain the thermal evolution. In order to facilitate part of this study a thermodynamic analysis has been performed on selected phases in the system $KCMASH_2OCO_2$, in order to calculate geologically useful reactions.

1.2 REGIONAL GEOLOGY & STRATIGRAPHY

The area under consideration comprises that affected by the late Cambrian to Ordovician Grampian Orogeny. In Scotland this area is bounded to the south by the Highland Boundary Fault and to the north by the Moine Thrust (figure 1.1), the effective northwestern limit of Grampian metamorphism and deformation. Two supergroups are represented, the Dalradian and Moine, the latter of which is polyorogenic. Both these supergroups are also represented in the north of Ireland.

The Dalradian (figure 1.2) is overlain unconformably by Devonian Old Red Sandstone. In the south, it is bounded by the Highland Boundary Fault, along which a suite of ophiolitic rocks, the Highland Border Complex is found. This suite may be of Dalradian (Henderson and Robertson, 1982; Ikin and Harmon, 1984) or post Dalradian (Curry et al., 1982) age. It has been suggested that this complex originated within an intra Dalradian basin and was emplaced from the north (Henderson and Robertson, 1982 c.f. Curry et al., 1982). In the north the Dalradian is in slide contact with rocks of the Moine Supergroup (e.g. Roberts and Treagus, 1979). Geophysical work (Bamford et al., 1977) and petrogenetic studies of post orogenic granites (Pidgeon and Aftalion, 1978; Hamilton et al., 1980) suggest that the Dalradian is underlain by high grade basement of Lewisian (>2000Ma) or Grenvillian (1000Ma) origin.

The Dalradian was deposited between ca. 700Ma and the Cambrian/ early Ordovician. Lower Cambrian fossils are known from the Southern Highland Group (Harris and Pitcher, 1975).

It has been suggested recently that Pre-Cambrian basement gneisses are represented within what was previously considered to be a Dalradian tract in northeast Scotland (Sturt et al., 1977; Ramsay and Sturt, 1979). This proposed allochthonous basement slice has been termed the Banff Nappe (Ramsay and Sturt, 1979). Its recognition was based on two observations:

(1) earlier phases of deformation are believed to be represented in the high grade gneisses of NE Scotland.

(2) Pre Grampian Rb-Sr whole rock isochrons of circa. 700Ma have been obtained from some high grade gneisses in the NE Dalradian (Sturt et al., 1977).

The first observation is insufficient evidence for a Pre Grampian basement slice. The early phases of deformation might relate to an early phase of the Grampian Orogeny. The Rb-Sr isochrons have very scattered points and

give poor dates. They probably do not represent strontium isotope homogenisation during a pre-Grampian metamorphic event. The difficulty of such homogenisation during an amphibolite facies metamorphic event has been emphasised by Magaritz and Hoffman (1978). The isochrons might represent diagenetic ages. In addition, it is proposed that a Dalradian stratigraphy is recognisable within the supposed basement slice (Ashcroft et al., 1984)

Dalradian Basin Evolution

The sedimentary history of the Dalradian has been reviewed by Harris et al. (1978) and by Anderton (1982). It is summarised in figure 1.3. The lower part of the Dalradian (up to the Jura Quartzite) comprises relatively thin laterally persistent shelf and marginal marine sediments. The upper parts of the Dalradian consist of deep basinal and turbiditic facies associated with volcanics. These are not laterally persistent and were deposited during syndepositional faulting. This is interpreted as indicating increasing basin instability upwards within the Dalradian during basin stretching (Anderton, 1982).

It is undoubtedly the case that the Dalradian is presently underlain by pre Grampian basement. However, it is uncertain whether early Dalradian evolution was entirely ensialic, as advocated by Harris et al. (1978), or whether it is possible that some oceanic crust was present. Possible ophiolites have been suggested to occur within the Dalradian (Garson and Plant, 1973) and the occurrence of serpentinite melange within the Dalradian of the west of Ireland suggests a partially oceanic basement (Kennedy, 1980). Henderson and Robertson (1982) suggest an intra Dalradian origin for the ophiolitic Highland Border Complex. Volcanic rocks within the Dalradian comprise Fe and Ti enriched tholeiites which have spreading centre affinities (Graham and Bradbury, 1981). Some of the turbiditic facies of the Upper Dalradian (Southern Highland Group) must have been

derived from a southerly source, as indicated by their immaturity and by the difficulty of transporting them across the extensive shelf carbonates to the northwest. Various palaeocurrent evidence supports such a northern source. These observations have led to the inference of a presence of a southern landmass, perhaps now removed by strike slip motion (Anderton, 1982; Yardley et al., 1982).

The Moine

The Moine Supergroup comprises a polyorogenic series of metasediments. The northern Moines are separated from the southern Grampian Moines by the Great Glen Fault. The ages of the various orogenic events within the Moines is controversial. Grenvillian events (ca. 1000Ma) certainly occurred in the northern Moines (Brook et al., 1976 ; Brewer et al., 1979), but the reality of a Morarian orogenic event (~750Ma) is the subject of debate. Pegmatites of this age are recorded from the northern Moines (vanBreemen et al., 1979) and from the Grampian Moines (vanBreemen and Piasecki, 1979). Circa 750Ma Rb-Sr whole rock isochrons from the northern Moines may represent a Morarian isotopic rehomogenisation (vanBreemen et al., 1978) or Grampian resetting of a Grenvillian isotopic system (Brewer et al., 1979). The evidence for a Morarian orogeny rests upon a dated pegmatite suite, which by itself does not imply an orogenic event and some whole rock dates of uncertain significance (Powell et al., 1983).

In the northwest, the Moine is thrust over Lewisian basement and Cambrian platform carbonates along the Moine Thrust. This represents the effective northwesterly limit of major Grampian thermal and deformational events. The Lewisian basement and Cambrian carbonates represent the NW foreland of the Grampian Orogeny.

Major Faults

The area under consideration is bisected by the Great Glen Fault and associated subsidiary faults. Movement on these faults was sinistral (Johnson and Frost,1977). Considerable (~2000km) post orogenic Devonian strike slip has been suggested on the basis of palaeomagnetic evidence (vander Voo and Scotese,1981). This is not supported by more recent palaeomagnetic work (Turnell and Briden,1983; Briden et al.,1984) or by geological evidence (Smith and Watson,1983). For instance, Lewisian basement is found on both sides of the fault.

In the south the extension of the Highland Boundary Fault into Ireland is defined geophysically (Max and Riddihough,1975). Some Dalradian elements such as Connemara which lie to the south of this line may have been emplaced to the south during the Grampian Orogeny (Leake et al.,1984).

1.3 THE GRAMPIAN OROGENY

Dalradian and Moine sediments were deformed and metamorphosed during the late Cambrian to Ordovician Grampian Orogeny (Lambert and McKerrow,1976). Events to the northwest of the Great Glen Fault occurred later in the Ordovician (vanBreemen et al.,1979a ;van Breemen et al.,1979b) than to the southeast. Recently such later events have also been recognised in the Grampian Moines (Piasecki and vanBreemen,1983). These differing ages of orogeny may relate to a diachronous Grampian Orogeny or to a juxtaposition of areas of different orogenic history along the Great Glen Fault.

The mechanism which led to the initiation of the Grampian Orogeny is enigmatic. Various collisional events have been postulated (Lambert and McKerrow,1976; Dewey,1982) or alternatively an Andean type evolution is envisaged (Phillips et al.,1976; Yardley et al.,1982). If an Andean type model applies and no major collisional event occurred then the high

pressures recorded in some Dalradian rocks must presumably have been achieved within a subduction zone. Various types of collisional event have been suggested. Lambert and McKerrow (1976) have suggested the impingement of a mid ocean ridge which may have provided a heat source for the high temperature metamorphism. Dewey (1982) suggests a seamount while Mitchell (1984) advocates collision with an arc. Dewey and Shackelton (1984) suggest that the orogeny resulted from the obduction of an ophiolite nappe.

1.4 STRUCTURAL MODELS

A generalised structural cross section of the Grampian Orogenic Belt is shown in figure 1.4. A number of different structural models are currently proposed for the Dalradian. A brief outline will be given of the general structural features of the Central Highlands and the various syntheses which are proposed. Generally, the Grampian Orogeny resulted in NW directed thrusting and sliding. This NW-SE convergence was reflected by steep SE dipping lineations in slide zones (e.g. Shackelton and Ries, 1984).

The southern part of the Dalradian outcrop is characterised by the lower inverted limb of the southeast facing Tay Nappe. Within this limb stratigraphic dips are subhorizontal. The southern margin of the 'flat belt' is marked by a belt of steeply dipping foliation and stratigraphy adjacent to the Highland Boundary Fault, the Highland Border Steep Belt. To the north of the flat belt lies another steep belt, the Tummel Steep Belt. Still further to the north the stratigraphy is dominantly the right way up and folds and slides verge towards the northwest (e.g. Bradbury et al., 1979; see figure 1.5a).

This picture may be modified to the northeast and to the southwest. To the southwest higher structural levels are reached in the Loch Awe Syncline (see figure 1.5b). To the northeast the Buchan area is of uncertain status. It is proposed that it comprises an allochthonous slice

of Pre Cambrian basement (Ramsay and Sturt,1979), an allochthonous nappe of later rocks (Ramsay and Sturt op.cit.) or an autochthonous area (Ashcroft et al.,1984). To the west of the possible Banff Nappe (comprising the Buchan area) a number of NW verging slides are found analogous to those in the Central Highlands. The structural relationships between the Tay Nappe and the Banff area are enigmatic.

Some models note that there is a change in dominant fold vergence across the Tummel Steep Belt from southeasterly in the south to northwesterly in the north. This has led to the suggestion that the steep belts represent root zones from which nappes of opposing vergence were expelled (Sturt et al.,1963; Thomas,1979 figure 1.6). This model assumes the correlation of fold phases of opposing vergence across the steep belt.

An alternative is to interpret the steep belt as a rolling hinge about which the Tay Nappe was translated to the south (Bradbury et al.,1979). In this instance northwest verging folds and slides to the northwest of the Tummel Steep Belt are believed to be later than Tay Nappe formation. Other workers do not follow the rolling hinge model, but agree that the Tummel Steep Belt is not a root zone (e.g. Roberts and Treagus,1979).

Structural chronologies are recognised in a number of areas. Many attempts have been made to establish a structural reference frame for large parts of the Dalradian (see table 1.1). There are a number of disagreements between the different deformational chronologies and their correlation. Many of the correlations seem hard to establish e.g. those between the Tay Nappe flat belt and areas further to the northwest.

1.5 METAMORPHISM

The metamorphism of the Scottish Dalradian has been reviewed by Atherton (1977) and that of the Irish Dalradian by Yardley (1980). Much

of the classic work on isograds and mineral zones was done in the Scottish Highlands (Barrow, 1893; Tilley, 1924). The disposition of mineral zones in the Scottish Highlands is shown in figure 1.7, modified after Atherton (1977). The classic Barrovian metamorphic sequence characterised by garnet, staurolite, kyanite and sillimanite zones was originally mapped by Barrow (1893). Since then a number of other facies series have been recognised in different parts of the eastern Highlands (Harte and Hudson, 1979; figure 1.8). In the northeast along the Buchan coast low pressure, andalusite and cordierite bearing, facies series are found (D & E of Harte and Hudson). In areas of intermediate pressure such as the Stonehaven Coast AFM chloritoid-biotite assemblages are found (C of Harte and Hudson). In the Central Highlands a Barrovian type sequence is present, but sillimanite does not occur.

The eastern Dalradian is characterised by a development of all three aluminosilicate polymorphs. Andalusite occurs in the Buchan area and kyanite to the west and in the Barrovian zones. An andalusite-kyanite isograd exists between these two areas. An attempt to define this isograd has been made by Chinner and Heseltine (1979), but its recognition is complicated by the presence of much contact metamorphic andalusite.

Over much of the eastern Dalradian sillimanite coexists with either andalusite or kyanite in a zone of overprint. Chinner (1966) suggested that a separate metamorphic event, an isobaric temperature rise led to the sillimanite overprint. This overprint is now generally believed to be part of a progressive metamorphic event (Harte and Hudson, 1979; Chinner, 1980).

Recently attempts have been made to estimate quantitatively the values of pressure and temperature during metamorphism. These attempts have been based on the calibration of isograds or on direct thermochemical methods. Harte and Hudson (1979) attempted to calibrate isopleths based on

a number of continuous mineral reactions and considered their intersection with aluminosilicate isograds. On this basis, they drew a set of isobars and isotherms covering the eastern Dalradian. Wells and Richardson (1979) used thermochemical methods in the Central Highlands and obtained very high pressures ranging from 8kb to 12kb. These are considerably in excess of the pressures estimated by Harte and Hudson, although the areas considered by the two authors are little separated geographically (figure 1.9 and table 1.3).

Little work has been done on possible P-T paths for Dalradian rocks. An isobaric overprint model has been suggested to explain the development of sillimanite after andalusite and kyanite in the eastern Dalradian. In contrast Wells (1979) suggests that much Dalradian sillimanite was developed during decompression of the warming pile.

Debate has also centred around the possible presence of inverted isograds within the Tay Nappe. An inverted garnet isograd was originally mapped in the Central Highlands by Tilley (1925) and remapped by Watkins (1984). Chinner (1980) also asserts an inverted kyanite isograd within the eastern Highlands. In contrast, Harte and Hudson (1979) suggest more steeply dipping isograds.

Much effort has been directed at establishing the relationships between deformation and porphyroblast growth in different parts of the Dalradian. These relationships are summarised in table 1.2. It is emphasised that no correlation is implied between local phases of deformation denoted by the same numeral.

1.6 IGNEOUS ACTIVITY

A number of suites of igneous rocks have been recognised within the Dalradian and Moine. The distribution and age of these rocks is summarised in table 1.4 and in figures 1.10 through 1.12. The Older Gabbros are a series of variably deformed and metamorphosed mafic bodies and

serpentinites. They are distinguished by a lack of contact metamorphic hornfelses. The Newer Gabbros are a group of synmetamorphic bodies restricted to the Buchan area of NE Scotland. They are associated with contact metamorphic aureoles and may ^{have} been a significant heat source (e.g. Ashworth, 1975).

Synmetamorphic and early post metamorphic granitic intrusions are of fairly small volume and are believed to have been derived by crustal anatexis (Brown et al., 1981; Pankhurst and Sutherland, 1982; Clayburn, 1981). They are two mica granites without hornblende and correspond to S type granites of Chappell and White (1974). They occur at about 470Ma in NE Scotland and at about 445Ma in the Grampian Moines.

A further suite of post orogenic granites occurs at about 400Ma (the Newer Granites) and comprises a calc alkali suite, often with an early diorite marginal to a later hornblende-biotite granodiorite-tonalite (Brown et al., 1981; Pankhurst and Sutherland, 1982). Calc alkaline andesites and rhyolites are also found (Thirlwall, 1981). These late granites are believed to comprise a component of mantle origin, as well as extensive lower crustal contributions (Clayburn, 1981; Pankhurst and Sutherland, 1982). They may be related to subduction to the south and east of the Scottish Highlands (Thirlwall, 1981). These intrusions generally have well developed contact metamorphic aureoles. Geobarometry of these aureoles may potentially provide information on the uplift history of the area.

1.7 GEOCHRONOLOGICAL DATA

Geochronological evidence is presented in order to establish the timing of different events throughout the Grampian Belt. Constraints on the age of metamorphism are summarised in table 1.5 and on the age of deformation in table 1.6. Locations mentioned are shown in figure 1.13. Generally it appears that there is a SE to NW diachroneity of peak

metamorphic and deformational events, commencing in the southeast at 520Ma and terminating in the northwest at 450M to 430Ma.

Approaches to determining structural correlations and the relative timing of thermal events in different areas will obviously have great bearing on models designed, to explain the evolution of orogenic belts. It is appropriate, at this stage, to examine the methodology that may be used, and implications to our understanding of the Dalradian. A discussion on these points *constitutes* the remainder of this chapter.

1.8 CORRELATION

Deformational events in metamorphic belts are commonly correlated on the basis of similar style, fabric, fold symmetry and orientation. It is questionable whether such correlational procedures can successfully establish the synchronicity of deformational and hence of thermal events across an orogenic belt. Park (1969) has discussed the validity of the various criteria which might be employed. Fold style is of little value in correlation as it is likely to be related to factors such as lithology and local intensity of deformation. Similar fabrics and foliations relate to similar thermal conditions which may occur in different places at different times or in the same area over a long period of time. Fold symmetry is of little use as it will reflect the interaction of prefold geometry and the stress field. Correlations implied by similar orientations depend upon the premise that a given stress field is contemporaneous everywhere and is not long lived. This may not always be the case (e.g. Butler,1983). There is thus no sound theoretical basis for the correlation of deformational events in metamorphic belts except very locally. Unrelated deformational events widely separated in time may produce structures of similar orientation that are apparently correlatable (Tobisch and Fiske,1981; Roberts and Sanderson,1971; Saleeby and Sharp,

1980). These examples arise in relatively low grade areas. Presumably similar complications are at least equally likely to arise in higher grade areas.

Problems of fold or foliation correlation are considerably enhanced, now that thrust tectonic models emphasise that structural units now juxtaposed, may originally have been very widely separated. Studies of thrust belts show that shortening of ~100km or more may occur along many thrust systems (e.g. Brewer and Oliver, 1980). It cannot be generally valid to correlate early phases of deformation between areas, that may initially have been so far apart.

Sequential overprinting relationships may sometimes be related to progressive deformation, rather than to unrelated deformational events (Williams and Zwart, 1977; Jacobson, 1983). Bell and Rubenach (1983) describe various structures related to progressive deformation and locally variable strain. Apparent overprinting relationships are related to progressive refolding in higher strain zones, rather than to a series of sequential deformational events.

Conversely one individual deformational event may produce structures of widely differing orientation. For instance Ramsay et al. (1983) describe folds from the Alps that develop initially in an upright orientation, but are then rotated into a subhorizontal position and become isoclinal in zones of more intense deformation. Both upright open folds and recumbent isoclinal folds are related to the same shearing deformation. Fold orientations can be related to local stress fields and hence be of uncorrelatable character.

Even if a deformational event may be correlated over a wide area it may not be reasonable to assume that this event was effectively instantaneous. It may be that the event is related to a geologically long lived stress field and that strain happened in different places at

different times. Many studies have demonstrated the sequential migration of thrusts towards the foreland over long periods of time (e.g. Price and Mountjoy, 1970). The periods of time during which such thrusting events may continue is considerable. In the Canadian Rockies Thrust and Fold Belt thrusting spanned ~100Ma (Price, 1981). In the Central Alps it may have lasted about 50Ma or more (Hsu, 1979; Milnes and Pfiffner, 1980). In the Himalayas thrusting events still continue today. In the Appalachians thrusting spanned a considerable period of time including the metamorphic peak although this is in part related to separate orogenic events (Hatcher and Odom, 1980). It seems reasonable to assume that similar diachroneity accompanied deformation phases in the Grampian Orogeny. The geochronological data summarised in an earlier part of this chapter indicate that this is so.

1.9 METAMORPHISM

The enlightening thermal models of England and Richardson (1977) imply considerable diachroneity in the attainment of peak conditions of regional metamorphism. They envisage a model involving crustal thickening by instantaneous overthrusting, followed by self heating during isostatic uplift and erosion. It is predicted that different rocks will reach their peak metamorphic temperatures at different times, according to their initial depth in the thickened pile. Diachroneity in this model is related to initial depth within the pile. This type of model has been applied to the Grampian Orogeny by Wells (1979). He suggests that Dalradian metamorphism may be diachronous as a result of regional variation in uplift rates and initial crustal thicknesses.

The England and Richardson (1977) sort of model applied to relatively large areas of orogenic belts requires effectively instantaneous thickening across the belt (e.g. see Wells, 1979). It might be suggested that thickening is likely to occur at different times across an orogenic

belt during a long lived crustal restacking process. Different tectonic units might be expected to follow different and quite complex P-T-t paths during continued reshuffling of these units.

Thermal relaxation to maximum temperatures takes, perhaps, about 40Ma after tectonic thickening (e.g. England,1978). Indications are (see above) that deformation across an orogenic belt typically spans a period of the order of this length of time. If this is correct and important deformational events are continuous over considerable periods of time then the following conclusions are implied:

(1) uplift paths of individual tectonic units might be expected to be tectonically, rather than isostatically controlled. For instance Dempster (1984) has shown that uplift is not isostatically controlled in the Dalradian. Tectonically controlled uplift paths are required, in order to explain the preservation of many eclogites and blueschists (Cuthbert et al.,1983; Rubie,1984). This is not to imply that post tectonic uplift is not isostatic.

(2) crustal thickening will be diachronous across an orogenic belt. Metamorphism across the belt will be more diachronous than would be suggested by the simple England and Richardson or Wells models. It might also be possible that individual tectonic units might not experience instantaneous thickening. Such diachroneity as this is incorporated into the models of Ernst (1975) for subduction zone metamorphism.

Evidence of such long lived crustal thickening events is provided by the relative timing of the beginning of deformation and the beginning of the deposition of the clastic wedge relating to the orogenic event. Several tens of millions of years may be required before the thickening tectonic pile is high enough to induce such sedimentation. This may be explained if the crust is thinned during preorogenic basin formation and then restacked and thickened over a long period of time (Dewey,1982).

It is observed that in many orogenic belts a series of isograds within a facies series may be inverted (e.g. Chinner,1980; Sinha Roy,1982; Andreasson and Lagerblad,1980; Mason,1984). Facies series may also have very high preserved thermal gradients (e.g. Harte and Hudson,1979; Brynhi and Brastad,1980; Tracy and Robinson,1980). These observations suggest the occurrence of long lived deformational events. In the absence of continuing deformation such inverted and high thermal gradients will rapidly decay. Continued underthrusting is required in order to preserve such gradients. An extreme case is that of the "freight train" model for the metamorphism of ophiolite soles which are clearly not explainable in terms of static models. Rocks of progressively lower grade are accreted to the base of the ophiolite as it is thrust from mantle to upper crustal levels. This results in a sequence of decreasing pressure and temperature away from the base of the ophiolite (Spray and Williams,1980; Ghent and Stout,1981). A similar model might apply to broader inversions of metamorphic zonation in more conventional regional metamorphic settings.

It may be useful to consider metamorphic evolution across an orogenic belt with respect to different thrust type tectonic models, as applied to the internal zones of orogenic belts (e.g. Coward,1983a). A given tectonic unit will be buried as a result of thrusting and ductile deformation and will be later exhumed, as the result of more external thrusting. This more external thrusting might produce uplift more rapid than isostatic. Internal structural elements as well as metamorphic isograds will deform and steepen as a result of more external thrusting.

It is relevant to consider the interpretation of facies series shapes with respect to these models. England and Richardson (1977) consider in their model "small areas subject to considerable local structural relief". If many facies series represent tectonic boundaries or shear zones

in which active synmetamorphic deformation is occurring facies series shapes may be hard to interpret. The extreme case would be that of an ophiolite sole. The facies series shape in this instance would require dynamic modelling with synmetamorphic deformation. It might be questioned how often the conditions, required by the England and Richardson (1977) model apply locally and how valid it is to use the shape of facies series as diagnostic of a given metamorphic process.

Summary

Data from different orogenic belts suggesting that thrusting and deformation are long lived events, often lasting longer than the time required to reach peak metamorphic temperatures after crustal thickening. The continuity and long lived nature of the thrusting is evidenced by inverted and high thermal gradients. The assumption of instantaneous crustal thickening across an orogenic belt (Wells, 1979) is not likely to be correct. Crustal thickening if it is diachronous by several tens of millions of years across an orogenic belt will induce similarly diachronous thermal peaks. Different tectonic units may be expected to have vastly different P-T-t paths and metamorphism will be expected to be very diachronous across a belt.

The operation of continuing deformation and long lived thrusting in orogenic belts is evidenced by:

- (a) preservation of high pressure rocks.
- (b) preservation of inverted and high thermal gradients.
- (c) strongly diachronous metamorphism.

and is implied by constraints on the timing of deformation.

1.10 THERMAL AND TECTONIC REFERENCE FRAMES

The dating of porphyroblast growth with respect to deformational events is a common practice in metamorphic belts and has been applied to a

great extent in the Dalradian. The contention that both metamorphism and deformation are considerably diachronous in orogenic belts must be taken into account when applying this methodology.

Two extreme procedures might be adopted (e.g. Chadwick, 1968):

(1) assume a given deformational event is instantaneous over the study area and date periods of porphyroblast growth with respect to it.

(2) assume that the peak metamorphic event is instantaneous over the study area and date different tectonic features with respect to the metamorphism.

The discussions in the earlier part of this chapter suggests that neither of these assumptions is always correct. Certainly neither can be expected to be perfect, except very locally. On a small scale within one individual tectonic unit, it is presumably reasonable to assume that metamorphism was instantaneous and therefore the local dating of deformation with respect to metamorphism is considered valid. Local correlation of deformation phases is also likely to be reasonable. It is interesting to compare these two approaches over a very small area, where different stages in the metamorphic evolution are preserved. Such an instance is described by Boudier and Nicolas (1976). They adopted the procedure of correlating deformation events with respect to stages in the metamorphic evolution. Apparently similar and correlatable events on the grounds of orientation prove to have occurred at different times, as indicated by their relationship to stages in the progressive metamorphic evolution.

Summary

In conclusion the following points might be made:

(1) The correlation of deformational events over wide areas does not necessarily imply that strain was synchronous.

(2) Correlated deformational events may sometimes be totally unrelated. In appropriate circumstances wider scale correlations may be permissible, although it is difficult to suggest criteria by which to select these circumstances.

(3) It is unwise to date periods of porphyroblast growth with respect to phases of deformation except locally (e.g. Vernon, 1978).

(4) It is sometimes useful to use metamorphism as a reference frame locally perhaps within one tectonic unit, but not over wide areas.

(5) Metamorphism may be expected to be strongly diachronous, both as implied by the simple models of England and Richardson (1977) and as a consequence of potentially strongly diachronous crustal thickening and uplift across a belt.

1.11 THE GRAMPIAN OROGENY: DIACHRONEITY

As a consequence of the above discussion the following inferences are made concerning deformation and metamorphism in the Grampian belt. It has been assumed that porphyroblast growth in Buchan and Barrovian areas was contemporaneous. This has been concluded on the grounds of correlation of deformation phases between Buchan and Barrovian areas, at least partly on the basis of chronology. This inferred synchronicity is considered to be unlikely. Diachroneity is to be expected rather than the reverse. Another problem is the timing of sillimanite growth relative to metamorphism in other areas. Conventional Dalradian wisdom would suggest that it is later than metamorphism elsewhere on the grounds of its relationship to a supposed synchronous and correlatable D3 deformation (e.g. McLellan, 1984). Eastwards passage of a heat source has been inferred on the grounds of western syn D3 sillimanite and eastern post D3 sillimanite. There is no justification for this assertion. Deformation and metamorphism are both likely to be diachronous. Inferences concerning the timing of porphyroblast growth by tying this growth to a probably diachronous phase

of deformation must be treated with caution. It is probable that different tectonic units, which may have been widely separated until a relatively late stage in the Grampian Orogeny, experienced vastly different P-T-t paths.

Correlation of deformation phases over the Dalradian and Moine has lead to symmetrical mushroom style models for the tectonic evolution (e.g. Sturt,1963; Thomas,1979). Nappes of opposing SE and NW vergence are envisaged as emerging fountainwise from central steep belts. No reason is seen by the author to correlate early nappe forming events between Grampian Moines and the Dalradian. Coward (1983b) has pointed out some of the problems with such correlations and has suggested that nappes of opposing vergence may develop at different times. The rigid separation of Dalradian structural events into 3 or 4 separate individual deformation phases is probably too rigid and hampers the development of imaginative models for the structural evolution. Correlations based purely on the inflexible assumption that there are only three separable deformational events which are capable of being widely correlated are regarded with some scepticism.

Models in which diachroneity of metamorphism is predicted, as a consequence of initial depth in the pile and rate of erosion (Wells,1979), are likely to underestimate the degree of diachroneity. Regional syntheses of the variation of metamorphic temperatures and pressures, based on the intersection of isopleths, are probably erroneous as these isograds may be expected to be considerably diachronous.

It is suggested that a number of common assumptions regarding the extent of diachroneity of metamorphism and deformation in the Dalradian should be reexamined. The structural correlations proposed by some authors in the past are likely to be misleading.

CHAPTER 2

GENERAL PETROLOGY

In this chapter a brief summary will be given of mineral assemblages, relevant petrographical information and the mineral chemistry of metapelites and metabasites from the various areas studied in the Dalradian. A number of empirically useful continuous reactions will also be considered. Metapelites and amphibolites have been collected from a wide area of the Dalradian aluminosilicate zones. Details of assemblages are given in tables 2.1 and 2.3 and in the appendix.

Metapelitic rocks have been studied from the low kyanite to the sillimanite K feldspar zone. Typical textures within the kyanite zone are illustrated in figures 2.2 and 2.3. In the lowest part of the kyanite zone the rocks are graphitic schists with a fine muscovite biotite schistosity. In the higher part of the kyanite zone the schistosity is coarser. Porphyroblast phases; garnet, staurolite and kyanite are often syntectonic and show rotated inclusion trails. In the higher grade areas migmatites occur. These are hypothesised to be both the result of solid state differentiation processes and partial melting (McLellan, 1984). At the highest grades encountered the rocks are sillimanite bearing gneisses that have undergone extensive migmatization.

2.1 MINERAL ASSEMBLAGES AND ZONES: METAPELITES

The extent of the stability of various assemblages is illustrated in figure 2.1. Most of the area lies within the kyanite, sillimanite or andalusite zones as defined by the AFM assemblage aluminosilicate-staurolite-biotite or higher grade staurolite absent assemblages. Garnet chlorite assemblages are not stable over nearly the whole of the area studied. AFM Garnet-chlorite assemblages occur in Glen Avon and the Ailnack Gorge. In Glen Avon the AFM assemblage kyanite staurolite biotite is stable. However a number of AFM five phase assemblages contain garnet and chlorite. Although chlorite often lies within the schistosity (fig 2.4b) it is also axial planar to late microfolds and often replaces

garnet (fig 2.4a). The common occurrence of the five phase assemblage garnet-staurolite-kyanite-chlorite-biotite may reflect:

- (1) disequilibrium
- (2) buffering
- (3) the influence of additional components. For instance it is likely that garnet is stabilised by virtue of its grossular or spessartine component.
- (4) equilibration on a discontinuous reaction.

The water poor fluid composition estimated for these rocks in chapter 6 does not appear to be consistent with buffering.

In the Water of Ailnack kyanite is absent from AFM assemblages and has only been found in muscovite absent rocks (except where it coexists with retrogressive muscovite). AFM garnet chlorite assemblages occur with both muscovite and chlorite lying within the schistosity (fig 2.5). On the basis of two rocks showing the assemblage garnet-chlorite it is concluded that the Ailnack area lies in the garnet-chlorite zone.

In the Glen Ey area garnet chlorite assemblages occur only in muscovite absent calcareous metapelites which often contain margarite+quartz. Kyanite-biotite-garnet assemblages are common, but staurolite is absent. The area clearly lies within the kyanite zone. Similarly to the east in Glen Clunie kyanite biotite assemblages are found.

Metapelitic rocks on the Banff Coast, to the west of Portsoy, are generally of unsuitable composition to contain minerals diagnostic of a particular grade. It has been considered that much of the area lay within the garnet zone (see Atherton, 1977). However the sporadic occurrence of the assemblage kyanite staurolite-biotite indicates that the area is within the kyanite zone. No AFM garnet chlorite assemblages have been found.

Over the rest of the kyanite zone in the Central Highlands chlorite is only developed in garnet bearing assemblages as a retrogressive

product. The rocks studied in Glens Clova, Esk and the Duchray Hill Gneiss contain kyanite with or without fibrolitic sillimanite. Staurolite is stable over much of the area but not at the higher grades. The highest grade rocks in the Glen Muick-Cromar areas are described in chapter 3.

A number of other assemblages are of interest. Muscovite-calcite-zoisite-quartz is stable in limestones and more calcareous metapelites on the Banff coast (Peacock et al., 1968), Glen Avon, the Ailnack Gorge and in areas to the E and N of Glen Avon. The stability of this assemblage is illustrated in figure 2.6. The assemblage muscovite-calcite-quartz indicates a temperature maximum of 600°C.

Zoisite-rutile-calcite-quartz is stable in Ailnack and Glen Avon metapelites, indicating temperatures of less than 600°C. The stability of this assemblage is illustrated in figure 2.7. This has been calculated from the data of chapter 5, heat capacity, volume and entropy data for rutile and sphene from Robie et al. (1978) and the experiments of Jacobs and Kerrick (1981) at 6kb on this reaction.

Margarite+quartz appears to be stable in chlorite bearing metapelites in Glen Ey. It often occurs within pseudomorphs after kyanite. In some rocks a margarite schistosity is present, often enclosed within large late plagioclase porphyroblasts. In other instances margarite is in contact with quartz. This assemblage limits temperatures to a maximum of about 560°C at $P_{H_2O} = P_{TOTAL}$ (Chatterjee, 1976).

Paragonite-quartz has been found to be stable in Glen Avon (41A) and to the west of the Duchray Hill Gneiss (731). Its occurrence limits temperatures to not much more than aluminosilicate polymorph triple point temperatures at 4kb or less than 600°C at 6-7kb. Temperatures may be less in Glen Avon as plagioclase coexists with paragonite and quartz.

2.2 CHEMICAL MINERALOGY : METAPELITES

Garnet

Garnets may contain significant grossular or spessartine component, particularly at the lower grades. These components may result in the stabilisation of garnet outside what would be predicted in the pure KFMASH system (Harte and Hudson, 1979).

Representative zoning profiles are compiled in the appendix. Zoning profiles are of interest as a constraint on pressure temperature evolution. In the low kyanite zone grossular and spessartine components and Fe/Mg components generally decrease towards rims while pyrope and almandine components generally increase. In the higher grade areas (e.g. Glens Clova, Esk and the Duchray Hill Gneiss) zoning profiles are relatively flat. Compositions change sharply near the rims to lower grossular and higher Fe/Mg. This is assumed to result from high temperature homogenisation of zoning profiles followed by some retrogressive reequilibration. At lower grades zoning is more marked. At the highest grades in Glen Muick zoning profiles are fairly flat with manganese and grossular decreasing and almandine increasing slightly towards the rim.

Staurolite

Details of staurolite analyses are compiled in table 2.2 and in figure 2.8. Debate has centred around possible staurolite formulae, in particular the amount of water in the staurolite molecule. The following formulae have been suggested:

$(\text{Mg,Fe})_2\text{Al}_9\text{Si}_{3.75}\text{O}_{22}(\text{OH})_2$ (Richardson, 1968; Yardley, 1981; Pigage and Greenwood, 1982).

$(\text{Mg,Fe})_2\text{Al}_9\text{Si}_4\text{O}_{22}(\text{OH})$ (Naray Szabo and Sasvari, 1958)

The experimentally determined phase equilibria agree best with the first formula (Yardley, 1981; Pigage and Greenwood, 1982). The stoichiometries of

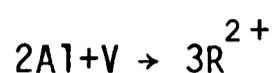
natural staurolites agree best with the second formula. The Al/Si ratio of the staurolites in this study has an average value of 2.26. However, this formula does not give a reasonable staurolite entropy, if an estimate is compared with that derived from the experimental work of Rao and Johannes (1979). All iron has been calculated as in the divalent state. When calculated in this manner $\sum \text{Fe} + \text{Mg} + \text{Mn} < 2$. This occurs if the analysis is recalculated to 23 or 23.5 (0). In figure 2.8 $\sum (\text{Fe} + \text{Mg} + \text{Mn})$ is plotted against Al' (aluminium remaining after subtraction of Al on tetrahedral sites), showing the correlation between these two parameters found by Griffen et al. (1982).

Biotite

Ca is normally below detection limits in the biotites analysed, Mn varies from about .01 to .2 wt%. Biotites generally contain much more aluminium than that appropriate to the annite-phlogopite join (fig 2.9). The substitution $\text{AlAl} \rightarrow (\text{Mg}, \text{Fe})\text{Si}$ is probably responsible (Rutherford, 1973). Analyses when calculated to 22(0) give consistently less than 14 octahedral and tetrahedral cations, suggesting the presence of vacancies (Dymek, 1983).

With grade the following compositional trends are noted. The titanium content of biotite in limiting assemblages increases from about 1.5wt.% in the low kyanite zone to 5wt.% in the sillimanite K feldspar zone. At higher grade the total K+Na is higher indicating the decrease of A site vacancy towards higher temperatures. It is uncertain to what extent vacancies on the A site are attributable to alkali loss during probe analysis. Alternatively chlorite interlayers might be present in the biotite structure at lower grades. Al(6) becomes lower in the higher grade rocks while Al(4) is not found to vary significantly. These variations are similar to those found by Dymek (1983) for amphibolite to granulite grade metapelites.

Al(6) is not balanced by Al(4) in excess of that required by the phlogopite-annite ideal formula in most of the biotites analysed. This must indicate the presence of some substitution such as



in addition to a tschermak substitution. Higher grade biotites in this study plot close to the line $\text{Al}(6)=\text{Al}(4)-1$, indicating that they are dominated by a tschermak substitution.

Muscovite

Muscovite has been analysed from metapelitic rocks from the low kyanite zone to just below the muscovite out isograd. Muscovites are plotted on a SAF diagram (fig 2.10) to show the extent of celadonite substitution. Muscovites contain up to 25% celadonite molecule. Muscovites from the low kyanite zone plot close to the muscovite celadonite join while at higher grades they scatter above this join. This may reflect substitution of trivalent iron for aluminium. Most muscovites analysed are deficient in alkalis, having less than a total of one alkali atom for 11 (O). This might be attributed to H_3O^+ substitution in the interlayer sites (Cipriani et al, 1971). However the low alkali analyses may reflect alkali loss on probe analysis. Muscovite shows a wide range in paragonite substitution with $x(\text{paragonite})$ ranging from 0.1 to 0.4. Margarite component is generally well below detection limits. Paragonite substitution decreases and titanium increases with grade. Possible A site vacancies decrease with grade.

Chlorite

The chlorites analysed are ripidolites with $\text{M}/\text{FM} \sim 0.5$.

Feldspars

Plagioclase compositions vary from anorthite 18 to anorthite 37 in metapelitic rocks apart from one analysis of anorthite 10. Typically

plagioclase compositions vary by a few percent over a thin section. More calcic plagioclases are found near garnet (e.g. W35) or plagioclases may be zoned to increasing anorthite contents adjacent to garnet (AB129 & AB135 in Glen Clova).

2.3 CONTINUOUS REACTIONS IN METAPELITES

A number of continuous reactions may be usefully employed to monitor changes in temperature, pressure and fluid composition. Where direct thermodynamic calibration of these reactions is possible this has been discussed in chapter 5. Two continuous reactions not capable of direct calibration will however be briefly considered here.

M/FM of biotite in Ky-St-Bi assemblages

The M/FM of biotite in the A F M assemblage kyanite staurolite biotite has been used as a monitor of metamorphic grade (Harte and Hudson, 1979; Chinner, 1980). Biotites become more ferroan with increasing grade. Calculations in chapter 6 suggest that these isopleths of biotite composition are very steep and almost pressure independent within the kyanite field. The data of this work, Chinner (1980) and Harte and Hudson (1979) shows that the M/FM of biotite in this assemblage varies from about 65 to 40 within the Dalradian kyanite zone.

Staurolite-biotite Fe-Mg exchange

Fe Mg exchange between staurolite and biotite and its variation with grade has been examined on the basis of data from the Dalradian. It is assumed that this exchange reaction will be temperature and not pressure sensitive. The fractionation is shown plotted against the garnet biotite thermometer of Ferry and Spear (1978) modified after Hodges and Spear (1982) (figure 2.11) and Ganguly and Saxena (1984) (figure 2.12). Staurolite biotite Fe-Mg exchange may be further constrained by examining data from other studies. These are shown in figure 2.13 and support the change in $\ln K_D$ s deduced from the Dalradian data.

The presence of varying $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the staurolites might result in an apparent variation of $\ln K_D$. Ten percent more Fe^{3+} staurolite than in biotite would result in a difference in $\ln K_D$ of only about 0.1. $\ln K_D$ varies from about 1.3 to 2.0. This variation reflects a variation in staurolite and biotite M/FM ratios (table 2.2). Staurolite Fe/Mg varies from about 2 to 6. It might be expected that staurolite solid solutions may be more ideal than garnet solid solutions, owing to the absence of substitutions, other than Fe for Mg.

$\ln K_D$ at triple point conditions for the exchange reaction seems to be about 1.56. The equivalent Hodges and Spear (1982) temperature of about 600°C appears too high to be appropriate to a low pressure temperature aluminosilicate polymorph triple point (see chapter 6). The Ganguly and Saxena (1984) modification of Ferry and Spear suggests temperatures of 550°C or less which is in reasonable agreement with preferred triple point temperatures. Coupled with the Ganguly and Saxena (1984) formulation of garnet biotite Fe-Mg exchange thermometry the following empirical relationship is obtained, which must be subject to great error.:

$$\ln K_D = (\text{Fe}/\text{Mg})^{\text{ST}} \times (\text{Mg}/\text{Fe})^{\text{BI}}, \quad \ln K_D = 0.00315T(\text{K}) + 4.24$$

No further calibration of the exchange reaction is possible owing to the lack of thermodynamic data.

In the Dalradian staurolite-biotite $\ln K$ s imply that the Buchan zones are hotter than those to the west in the kyanite zone. The Buchan zones are hotter than triple point conditions while the kyanite zone to the west appears to be cooler. Staurolite-biotite Fe-Mg exchange may be a useful constraint on grade within the aluminosilicate zone.

2.4 GARNET AMPHIBOLITES: PETROGRAPHY AND ASSEMBLAGES

A limited number of garnet amphibolites have been collected from the Dalradian aluminosilicate zones. A previous summary of these metabasites

is given by Wiseman (1934) which gives a more exhaustive summary of some assemblages and petrography. Assemblages are recorded in figure 2.3 and in the appendix.

Within the kyanite zone garnet amphibolites are dense homogenous rocks generally with a weak fabric. Within the sillimanite zone amphibolites are hornblende gneisses. Fine leucocratic stringers are intercalated with more mafic areas. These may represent partial melting of the metabasites. Plagioclase compositions and modal proportions of quartz to plagioclase are appropriate to such an origin (Yoder, 1967).

It is possible to distinguish a garnet clinopyroxene plagioclase quartz zone at the highest grades. These rocks occur in Glen Muick (see chapter 3) and also from the northeastern margin of the Duchray Hill Gneiss. The garnet clinopyroxene isograd occurs within the sillimanite zone. Chlorite occurs at the lower grades and gedrite occurs coexisting with a hornblendic amphibole in one Glen Clova amphibolite. Cumingtonite-hornblende appears to be stable in Glen Girnock.

Further examples of garnet clinopyroxene assemblages have been found outside the areas mentioned above. From the attenuated western aureole of the Morven Cabrach Newer Gabbro the quartz absent assemblage garnet clinopyroxene is found. In the Schichallion area Rast (1958) reports garnet clinopyroxene quartz. Examination of rocks from the locality which he reports show that the clinopyroxene is of relict igneous origin. Small garnets grow around the margins of these relict clinopyroxenes. Relict igneous textures are still visible.

Petrography

Modally most rocks are rich in hornblende which defines a variable fabric within the rock. In many rocks from the Central Highlands textures indicate that chlorite and epidote are late and possibly replacive of garnet.

A large number of rocks show evidence of garnet resorption. Very few rocks, except at the highest grades show euhedral garnets. They are usually very irregular and embayed. Garnets are very commonly surrounded by rims of plagioclase which separate the garnets from matrix hornblende. Such textures are found in the Central Highlands (746B, 740C, 752C, 752B, 752A, 749C, 747A, 747B & 747C) (figs 2.16, 2.17) and in one rock from Glen Esk (721A). In some cases garnets are totally replaced by plagioclase. This leaves circular areas composed almost entirely of plagioclase, with rare relict garnet fragments in the centre (Central Highlands: 746B & 752B, Glen Esk: 721A) (fig 2.18). In 747A the centres of resorbing garnets are replaced by plagioclase. In other instances zoisite appears to be involved in the replacement of garnet. In 740C and 752A garnets are replaced by plagioclase associated with zoisite and minor hornblende. Other rocks contain circular zoisite-plagioclase areas (plagioclase dominant) with no detectable relict garnet (723A: Glen Esk). The similarity of the texture with other textures, demonstrably the result of garnet resorption suggests that garnet was once present in these rocks as well. It appears that garnet amphibolites in the Central Highlands and in Glen Esk underwent reactions resulting in the growth of a reaction rim between garnet and hornblende and the replacement of garnet by plagioclase with sometimes more minor zoisite and calcite. These textures are similar in many respects to those described in chapter 8 resulting from the resorption of garnets in an amphibolitised eclogite in the Moine.

One rock from the north of the Duchray Hill Gneiss displays well preserved reaction textures. An early garnet clinopyroxene quartz assemblage is replaced by a later garnet-plagioclase-zoisite-hornblende-quartz assemblage. Garnets possess irregular cores with euhedral overgrowths. Zoisites surround garnet and clinopyroxenes are surrounded by hornblende. Zoisite is often intergrown with plagioclase in reaction

rims to clinopyroxene. The rock does come from quite close from a Newer Diorite margin. However it seems that garnet bearing assemblages are unlikely to occur in metabasites during the later lower pressure contact metamorphism. The rock is assumed to be of regional origin.

2.5 CHEMICAL MINERALOGY

Garnet

Garnets generally contain about 30% grossular component and 5% spessartine component. Representative zoning profiles are shown in the appendix. Grossular and spessartine components generally decrease towards garnet rims and Fe/Mg increases, at least in the high kyanite zone and above. In Glen Muick spessartine component increases towards the rim. At the higher grades garnets have flat profiles with rapidly varying compositions at the rims. In the Central Highlands somewhat irregular profiles may reflect garnet resorption (see above).

Plagioclase

Plagioclases analysed may contain from 40 to 80% anorthite component. Plagioclases are often zoned to increasing anorthite contents. In rocks where garnet resorption has occurred plagioclase in reaction rims to garnets seems to be considerably more calcic than plagioclase in the rest of the rock. In 752A it varies from An_{13} to An_{30} near garnet and in 747B it varies from An_{18} to An_{32} .

Amphiboles

Amphibole compositions are shown in figure 2.14. Amphiboles are pargasitic hornblendes (terminology of Leake, 1972). Titanium contents vary from 0.05 in the low kyanite zone to 0.30 molecules per 23(O) in the sillimanite K feldspar zone. Mn contents are very low. $K/(Na+K)$ is generally between 0.2 and 0.35.

Many amphiboles are fairly homogenous in composition. This may be the result of equilibration during active deformation. Where zoning is

detectable cores are rich in edenite and tschermak components while rims are richer in tremolite component.

Clinopyroxenes

Clinopyroxenes in amphibolites from Glen Muick and the Duchray Hill Gneiss are compositionally close to the diopside hedenbergite join with $M/FM \sim 0.6$. Aluminium contents are low, about 0.05 molecules of Al per 6(O).

2.6 AMPHIBOLE PLAGIOCLASE EQUILIBRIA

Two equilibria may be used to model reactions between hornblende and plagioclase and quartz:

- (1) $2\text{Albite} + \text{Tschermakite} \rightarrow \text{Glaucophane} + 2\text{Anorthite}$ (Spear, 1980)
- (2) $\text{Albite} + \text{Tremolite} \rightarrow \text{Edenite} + 4\text{Quartz}$ (Spear, 1981)

Data for the progress of these two reactions is shown in figures 2.15. Both equilibria are predominantly temperature sensitive (Spear, 1980, 1981). The diagrams are contoured with temperature estimates, obtained by independent means.

2.7 SUMMARY

The extent of the stability of the assemblage garnet-chlorite has been established within the aluminosilicate zones. Much of this chlorite may be of retrogressive nature, but its common occurrence in the Glen Avon and Water of Ailnack areas suggests that these areas lay close to the discontinuous reaction $\text{garnet} + \text{chlorite} \rightarrow \text{alsilicate} + \text{biotite}$. Some chlorite was certainly syntectonic.

Staurolite biotite Fe-Mg exchange appears to be strongly temperature dependent. This exchange equilibrium appears to provide an indication of relative temperature within the Dalradian.

The stability of:

paragonite+quartz

muscovite+calcite+quartz+zoisite

margarite+quartz

zoisite+rutile+calcite+quartz

in the lower parts of the kyanite zone show that temperatures must have been relatively low in these areas. Maximum temperatures for areas where these assemblages occur is 550°C to 600°C.

Metabasites from the Dalradian kyanite zone show textures indicating the resorption of garnet during progressive metamorphic evolution. A garnet clinopyroxene zone may be defined in metabasites. Garnet-clinopyroxene-quartz is stable in metabasites from the NW Duchray Hill Gneiss and Glen Muick.

CHAPTER 3

GEOLOGY OF THE GLEN MUICK AREA

FICHE AT

37

BACK OF THESIS

TO DUPLICATE

has been made of the Glen Muick and surrounding
north of Barrow's Zones (Harte and Hudson's 1979
sillimanite zone. The area under consideration
extends south to Cromar in the north, from Glen Tanar
to the west (figure 3.1). It sits astride the
boundary of Chinner and Heseltine (1979). Previous work
in the area has been carried out by Read (1928a &
1928b) who studied the Glen Esk and Glen Clova areas to

the area has been treated by Read (1928) and
Heseltine (1979). Dalradian stratigraphy in general is
discussed by Chinner (1975). Four stratigraphic units may be
identified in the area (figure 3.1 and table 3.1).

The limestone forms a narrow outcrop in East Glen Muick, but
extends further to the south. Its southward extent is not
clear because there are no outcrops of limestone to the southwest of
the area. However, the outcrop in the area is not good.

Stratigraphically below this limestone is found
the quartzite and Micaschist. To the east and
west is the Glen Tanar Group. To the west of the Queen's

Hill quartzite and Micaschist a further stratigraphic unit occurs,
separated by a belt of serpentinite and amphibolite from the Queen's Hill
Group. This is characterised by metapelite, psammite and calcsilicate
lithologies.

The Queen's Hill Quartzite and Micaschist consists of quartzites,
psammites, semipelites and pelites. Deformed granitic gneisses occur in a
few areas (e.g. N0333907 & N0405938). The rocks below the Deeside
Limestone in the Glen Tanar Group are more quartzose. Pelites are

A more detailed study has been made of the Glen Muick and surrounding area. This lies to the north of Barrow's Zones (Harte and Hudson's 1979 facies series A) within the sillimanite zone. The area under consideration ranges from Glen Mark in the south to Cromar in the north, from Glen Tanar in the east to Glen Girnock in the west (figure 3.1). It sits astride the andalusite-kyanite isograd of Chinner and Heseltine (1979). Previous work on the Glen Muick and Cromar areas has been carried out by Read (1928a & b). Harte and Johnson (1969) studied the Glen Esk and Glen Clova areas to the south.

3.1 STRATIGRAPHY

The stratigraphy of the area has been treated by Read (1928) and revised in part by Harte (1979). Dalradian stratigraphy in general is reviewed by Harris and Pitcher (1975). Four stratigraphic units may be distinguished in the study area (figure 3.1 and table 3.1).

The Deeside Limestone forms a narrow outcrop in East Glen Muick, but has not been located farther to the south. Its southward extent is not obvious. There appear to be no outcrops of limestone to the southwest of Hare Cairn (figure 3.2). However, the outcrop in the area is not good.

To the west of and stratigraphically below this limestone is found the Queens' Hill Quartzite and Micaschist. To the east and stratigraphically above is the Glen Tanar Group. To the west of the Queens' Hill Quartzite and Micaschist a further stratigraphic unit occurs, separated by a belt of serpentinite and amphibolite from the Queens Hill Group. This is characterised by metapelite, psammite and calcsilicate lithologies.

The Queens' Hill Quartzite and Micaschist consists of quartzites, psammites, semipelites and pelites. Deformed granitic gneisses occur in a few areas (e.g. N0333907 & N0405938). The rocks below the Deeside Limestone in the Glen Tanar Group are more quartzose. Pelites are

relatively minor. Correlations suggested by Read (1928) are shown in table 3.1.

Harte (1979) discusses the regional stratigraphy based on a study of the Glen Esk area to the south. He does not correlate the Deeside Limestone exactly with the Loch Tay Limestone, but suggests that the Loch Tay Limestone and Ben Lui Schist together are the correlatives of the Deeside Limestone and Glen Tanar Quartzite and Micaschist together. The stratigraphical relationships implied are detailed in figure 3.1. This compares with the alternative correlations proposed by Read (1928).

The gneisses of Glen Muick are stratigraphically distinct from the schists of Glen Girnock in that the latter contain considerable amounts of calcsilicate lithologies. The gneisses of Glen Muick seem to be stratigraphically correlatable with those of the Duchray Hill Gneiss to the southwest. The Glen Girnock lithologies might be compared with the Ben Eagach or Ben Lui schists, to the southwest (see Bailey, 1925). The Queens Hill Quartzite and Micaschist of Deeside and the gneisses of Glen Muick are very similar, suggesting their stratigraphic equivalence. They both lie above a thick belt of limestone and are composed in large part of psammitic and pelitic gneisses. Both have similar metamorphic rocks of equivalent grade, although in part obscured by later retrogressive metamorphism. The Queens Hill Micaschist and Quartzite of Deeside and the gneisses of Glen Muick are very similar and must be stratigraphically equivalent, as concluded by Read (1928a).

Most correlations equate the Queens Hill Quartzite and Micaschist with the horseshoe shaped outcrop of sillimanite gneisses to the northwest (Harris and Pitcher, 1975; figure 3.1). Sturt et al. (1977) have presented Rb-Sr whole rock strontium isochrons for these rocks giving dates of circa 700Ma. Thus Ramsay and Sturt (1979) interpret these gneisses as a slice of Precambrian basement thrust on top of part of the Dalradian and appear to

suggest that there is a tectonic boundary between the high grade gneisses of Glen Muick and those of Cromar. The gneisses of Glen Muick appear to correlate with those in the Duchray Hill Gneiss of accepted Dalradian age (Harris and Pitcher,1975). There is apparently stratigraphic continuity between the horseshoe of gneisses, Glen Muick and the Duchray Hill Gneiss. The correlations are inconsistent with a Precambrian age for some of the gneisses.

The Rb-Sr whole rock isochrons obtained by Sturt et al. (1977) are very poor with large scatters. They may not reflect isotopic homogenisation during a metamorphic event. The difficulty of homogenising strontium isotopes during an amphibolite facies metamorphic event is well known (Magaritz and Hoffman,1978). It might also be pointed out that similar Rb-Sr whole rock isochrons have been obtained from undoubted Dalradian rocks (Bell,1968; Pidgeon,1970). The ages may represent mixed provenance or diagenetic ages. It has recently become apparent that a Dalradian stratigraphy may exist within the horseshoe of sillimanite gneisses (Ashcroft et al.,1984). It is concluded that there is stratigraphic continuity through the Glen Muick-Duchray Hill Gneiss-Cromar areas and that therefore a Pre-Cambrian Banff Nappe is unacceptable.

3.2 LITHOLOGIES

Analytical and assemblage data are recorded in the appendices.

3.2.2 Metabasites

Metabasites are abundant in the area under consideration. These comprise garnet amphibolites, sometimes with clinopyroxene, metagabbros, epidote banded amphibolites and various sorts of retrogressed amphibolites. A number of rocks are cummingtonite bearing. Assemblages are detailed in figures 3.3, 3.4 and the appendix.

Garnet Amphibolites

A considerable area of Glen Muick contains outcrops of garnet amphibolite. These contain the maximum assemblage garnet-clinopyroxene-brown-hornblende-plagioclase-quartz-apatite-ilmenite-sphene-biotite. Biotite and sphene are absent from most examples and in any case are modally unimportant. A typical modal analysis is garnet 9%, clinopyroxene 8%, hornblende 46%, plagioclase 14%, quartz 19%, ilmenite and accessories 4%. Some examples may contain considerably more garnet and clinopyroxene than indicated by this mode.

The garnet clinopyroxene bearing amphibolites are recorded by Barrow and Cunningham-Craig (1913) from the hill of Cairn Leuchan. They have been discovered from a number of other areas. They extend along the ridge south of Cairn Leuchan as far as the aureole of the Lochnagar Newer Granite (figure 3.4) and as far west as the eastern side of the Coyles of Muick serpentinite and also as far SE as the hill of Hare Cairn. Further southeast amphibolites contain garnet, but not clinopyroxene. Occurrences have also been found from the northwestern part of the Duchray Hill Gneiss (see chapter 2).

Garnet clinopyroxene amphibolites in Glen Muick are typically dense homogenous medium to fine grained rocks. They contain lenticular clots rich in ferromagnesian minerals surrounded by anastomosing stringers of leucocratic material. The subparallel alignment of these clots gives rise to an indistinct foliation. Compositional banding is absent.

The mafic clots contain equigranular and polygonal clinopyroxene, brown primary hornblende and euhedral garnet (figure 3.5). Clinopyroxene often contains exsolution lamellae of orthopyroxene and may include all other mafic phases. Ilmenite is restricted to these mafic clots and is often intergrown with clinopyroxene. In one case this intergrowth surrounds sphene. Ilmenite rich areas sometimes form distinctive layers in

the rock (on a thin section scale). There is no petrographic evidence of any reaction relationships between phases apart from the ilmenite sphene textures and secondary blue-green hornblende that occasionally grows on clinopyroxene. Grain sizes of essential minerals are remarkably uniform throughout each rock and are generally .5 to 2mm. Textural indications are that equilibrium was achieved between these primary phases.

Textures are similar in other occurrences of clinopyroxene bearing amphibolites in Cromar, the Duchray Hill Gneiss and south of Glen Muick. In the Duchray Hill Gneiss clinopyroxene is modally less important and not ubiquitous in garnet amphibolites. In Cromar amphibolites occur on the hill of Craig Dhu (NN4901). These are garnet absent clinopyroxene amphibolites with large pale green clinopyroxenes. Read (1928b) does report some garnet bearing rocks, but these have not been located. One rock contains the texturally disequilibrium assemblage cummingtonite-tremolite-biotite-plagioclase-quartz-opaques. It contains a relict igneous texture. Cummingtonites are surrounded by randomly orientated biotites or the two minerals are intergrown.

The garnet clinopyroxene bearing mafic assemblage is interpreted as being representative of a high pressure subfacies of the granulite facies (Green and Ringwood, 1967). Schreinemaker's analysis of phases in the system CMAS confirms this view (figure 3.6). Orthopyroxene may be absent owing to the presence of calcic bulk rock compositions and/or rather high pressures. As such the assemblage is extremely unlikely to represent the effects of contact metamorphism from the many Newer Granites in the area. Most occurrences of this assemblage are well without the influence of any Newer Granite Aureoles. Clinopyroxene bearing amphibolites are reported from local Newer Granite aureoles, but contain the garnet absent assemblage clinopyroxene-orthopyroxene-hornblende (Chinner, 1962).

The presence of many anastomosing stringers of quartz and feldspar suggests that the rock may have been partially melted. The leucocratic stringers vary from finer concordant ones to larger ones which crosscut, but, but may be partially deformed. Deformation has not generally been strong enough to induce a foliation within the leucocratic material. The net veins and stringers are however compressed and subparallel to the foliation.

The composition of plagioclase in the stringers ($\sim\text{An}_{30}$) and the modal proportions of plagioclase to quartz ($\sim 60:40$) are appropriate to the origin of these stringers by melting processes (Yoder, 1967). It appears that melting synchronous with deformation has produced a complex series of net veins. The fact that many of these stringers have very mafic margins suggests that they are internally derived. The interior parts of these veins are often characterised by rather larger crystal sizes particularly of hornblende. This hornblende is compositionally similar to that in more mafic areas suggesting local derivation of the melt. The internal derivation of the melt is also suggested by the pervasive distribution and the ubiquitous presence of the veins and stringers.

Other Amphibolites in Glen Muick

Garnet absent metabasite assemblages also occur in Glen Muick. Some are of retrogressed origin, often with saussiturised plagioclase and epidote. Others are of peak metamorphic origin as indicated by their textural freshness. Retrogressed net veined amphibolites are shown in figure 3.7.

Amphibolites to the south of Glen Muick

At the southern margin of the area under consideration clinopyroxene is absent from garnet bearing amphibolites. The rocks have the same aspect in thin section, but are rather more deformed. They carry a stronger foliation. Hornblendes tend to be green rather than brown.

Metagabbros

To the west of Glen Muick a band of metabasites consist of a variety of lithologies including undoubted metagabbros with occasional coarse relict igneous textures. These contain the assemblage hornblende-plagioclase-quartz-opaques. They are variably deformed. Undeformed examples have little trace of a fabric although relict clinopyroxene is never present. Others are strongly lineated.

Epidote banded Amphibolites and others

Also associated with this band are a number of other amphibolite types. These contain the assemblage green hornblende-plagioclase-quartz-opaques with interspersed layers consisting of almost monomineralic epidotite with minor hornblende. Epidote bearing bands are a few mm across. The metabasites in this area never contain garnet or clinopyroxene. There is no evidence for migmatisation and no leucocratic stringers or veins.

Serpentinite

The band of amphibolite and metagabbro is also associated with a sizeable serpentinite body. It has not been studied in detail. Thin sections show a few remnant relict olivines, and one relict hornblende. Some talc-tremolite rocks have also been found from areas in east Glen Muick. They are of very small extent and may represent former ultrabasic rocks.

Chemical Mineralogy

In garnet clinopyroxene bearing amphibolites the following mineral compositions are found in a typical metabasite CL2. Garnet and clinopyroxene have homogeneous cores and rims of varying composition. Typical core compositions are Pyrope₁₄Almandine₆₀Grossular₂₄Spessartine₂ and Diopside₄₄Hedenbergite₃₆Enstatite₆Ferrosilite₅CaTs₄Jadeite₄Johannsenite₁ respectively. In garnet rims the Fe/Mg ratio and spessartine

component increase outwards while the grossular component decreases. In clinopyroxene the Fe/Mg ratio also increases (figure 3.8). Locally clinopyroxene rims have very high aluminium contents. The strong variation of compositions near mineral rims is interpreted as the result of uplift and retrogression on minerals of completely homogeneous composition. The primary brown hornblende is a ferroan pargasitic hornblende following the terminology of Leake (1978). Ilmenite is close to the ideal composition with little magnesium or ferric iron. There is considerable variation in plagioclase compositions from An₃₅ to An₅₅ over a whole thin section, but they are relatively constant locally.

3.2.2:Lithologies-Migmatitic Metapelites

Migmatitic metapelites (see figures 3.9 & 3.10) contain the maximum assemblage garnet-sillimanite-plagioclase-quartz-biotite-K feldspar-rutile. K feldspar is usually absent. Apatite also occurs. Many specimens show varying amounts of retrogression which may be attributable to late regional effects or to contact metamorphism. Sillimanite occurs in a variety of forms: fibrolite mats, aggregates of prismatic sillimanite or as separate individual sillimanites. Some of the prismatic sillimanite aggregates are probably pseudomorphous after kyanite. Al-silicate textures are detailed and discussed more fully in the next chapter. Garnets are usually non euhedral and are often partially resorbed. Most pelitic gneisses contain rutile. Others contain ilmenite in addition or instead of rutile. Ilmenite often occurs as a reaction rim to rutile or as separate grains associated with biotite grain boundaries. In some rocks rutile only occurs as inclusions within garnet (e.g. AB919A), while ilmenite occurs outside the garnet. Reactions may have occurred leading to the replacement of rutile by ilmenite.

Other minerals may occur in pelitic gneisses as a result of retrogression. Muscovite occurs in many rocks, but is believed not to be a

product of peak metamorphism. Chlorite often occurs in retrogressed gneisses, usually replacing biotite or garnet.

Most migmatitic metapelites show a prominent foliation (e.g. figures 3.10b & 3.11) defined by alternating quartz-feldspar rich leucosomes and garnet-sillimanite rich melanosomes, while others do not. In Cromar and around Cairn Leuchan there are areas of pelitic gneiss which are compositionally unfoliated. The rocks contains no strong fabric, but occasionally small shear zones are found. The assemblage is garnet-sillimanite-biotite-plagioclase-quartz-Kfeldspar-rutile. Irregularly shaped garnets are surrounded by areas rich in prismatic sillimanite and biotite (figure 3.10). In Cromar these aggregates are sometimes composed exclusively of biotite, ilmenite and sillimanite. Fibrolite is totally absent from these texturally fresh rocks. The presence of mafic and other xenoliths and schlieren within these rocks is evidence that these rocks have been partially melted. Xenoliths comprise:

- (1) mafic blocks.
- (2) quartzites and psammites.
- (3) aluminous pelitic material including relict schlieren (figure 3.12).
- (4) calc silicate xenoliths (Read,1928a).

The gneisses represent rocks in which migmatisation has reached an advanced stage. Where deformed these xenolithic pelitic migmatites consist of homogeneous compositionally unfoliated rocks full of plagioclase porphyroblasts. The term oligoclase porphyroblast gneiss was coined for these rocks (Barrow and Cunningham Craig,1913). Other such rocks have been found in Glen Mark and are reported from the Duchray Hill Gneiss (McLellan,1983).

Compositionally foliated migmatites are often not of simple stromatic layered type, but generally contain irregular shaped leucocratic segregations aligned within the foliation. Some rocks contain large

plagioclase porphyroblasts surrounded by melanocratic material. Other migmatites do possess a rather more well developed layered structure. As well as such fine scale segregations it is common to find larger pegmatitic and granitic segregations.

Debate often centres around the origin of migmatites, either as a result of solid state hydrothermal processes or as the result of partial melting. Yardley (1978) suggests criteria by which to distinguish the two. Layered migmatites in Glen Muick commonly possess basified peripheries to leucosomes which may be indicative of an origin by partial melting. It was also suggested by Yardley that leucosomes originating as partial melts should possess K feldspar and plagioclase more albitic than that in palaeosomes. Many Glen Muick and Cromar migmatites are trondjhemitic, not containing K feldspar. Plagioclase feldspar compositions are indistinguishable between leucosome and palaeosome. However both these criteria may not be useful (Ashworth, 1976; Johannes and Gupta, 1982). Modal analyses of leucosomes are compatible with the occurrence of partial melting. McLellan (1983) suggests that the plagioclase porphyroblast rocks (oligoclase porphyroblast gneisses or ophalmities) arise as a result of partial melting. In Glen Muick a range of textural types between plagioclase porphyroblast gneisses and rocks in which larger leucocratic segregations are developed is present. Partial melting may be convincingly demonstrated in the xenolithic gneisses of Cromar and Cairn Leuchan. It is concluded that the other migmatite types in Glen Muick mostly had a similar origin on the evidence of the discussions above.

Metapelites: Chemical Mineralogy

In typical metapelites garnets are pyrope almandine with minor grossular component. A typical composition is Pyrope₂₉Almandine₆₅Grossular₅Spessartine₁. They are roughly homogeneous with respect to grossular, but have increasing Fe/Mg ratios near the rims (figure 3.14).

Plagioclase compositions are approximately constant at around An₃₃. Biotites are relatively aluminous with between 1.51 and 1.71 Al atoms for 11(O) and have M/FM ratios of .52 to .56.

Other lithologies

In two areas (N0333907 & N0405938) deformed granitic gneisses have been found. Much of the area is composed of psammitic lithologies. These usually contain the assemblage garnet-plagioclase-quartz-opaques- biotite, some being very rich in quartz. Retrogressed examples contain muscovite or chlorite and partially resorbed garnets.

3.2.3 Metasedimentary Lithologies in Glen Gironck

To the west of the belt of serpentinite and metagabbro outcrops of a number of different lithologies occur (see figure 3.2 & table 3.4). Immediately to the west of these metabasites a belt of brownish weathering metapelitic schists occur. They contain the assemblage:

garnet-biotite-muscovite-quartz-plagioclase-staurolite-opaques (see figures 3.15 & 3.16). Kyanite occurs in three thin sections as large blades several mm long where it is surrounded by coarse muscovite in which sparse swirls of fibrolite are developed. Staurolite is often absent from the assemblage. A number of thin bands of amphibolite are interspersed with these schists. A fairly coarse muscovite-biotite schistosity is developed. Muscovite is clearly part of the equilibrium assemblage.

On the hill of Creag Phiobaidh calc silicate and psammitic lithologies occur. the latter contain plagioclase-quartz-muscovite-biotite-opaques. Calc silicates contain :

Calcite-Tremolite-Quartz-Biotite

Garnet-tremolite-quartz-plagioclase

and Clinopyroxene-Scapolite-Calcite-Sphene-Opaques

These calcsilicates continue on the west side of Glen Gironck around Camlet where they are infolded with metapelites and psammites.

Lithologies here include a tremolite rock consisting of large aggregates of radiating tremolite. Psammitic lithologies seem more common along the western side of Glen Girnock, metapelites in the east.

Metapelitic lithologies are often retrogressed. They may contain both andalusite and cordierite. Cordierite replaces garnet or occurs as reaction rims around staurolite. Andalusite overgrows the muscovite-biotite schistosity. Commonly new reddish biotites surround and replace garnet. These effects are interpreted as the effects of later contact metamorphism. Newer Granite material is intermixed as veins and apophyses with metasediments to the west of Glen Girnock (S of Camlet N0307924). In some instances clear contact metamorphic hornfelses are developed consisting of andalusite-cordierite-plagioclase-quartz-reddish biotite. The contacts of the Newer Granites may have shallow dips and underlie much of the Glen Girnock area.

3.3 METASOMATISM

It is notable that a large number of assemblages in Glen Muick migmatites contain neither muscovite nor K feldspar. These assemblages imply bulk rock compositions dissimilar to those indicated by muscovite-quartz bearing metapelites found ubiquitously in metapelites at lower grades. This suggests that metasomatism may have been operative. Potassium may have been removed from the rock during migmatization or as a result of fluid infiltration. Another possibility is that muscovite has been removed by melting reactions and did not reappear on reversal of these reactions for some reason.

A number of migmatized metapelites are very rich in aluminosilicates and garnet and contain little quartz and plagioclase. These extremely aluminous compositions are composed dominantly of aluminosilicate and probably result from metasomatism, perhaps the removal of a granitic melt. Retrogressed metapelites commonly contain large amounts of muscovite and

biotite often with little other material. These compositions may result from infiltration of potassium bearing fluids on a large scale. AB572D (N0359873) is extraordinarily rich in apatite.

3.4 RETROGRESSIVE METAMORPHISM

The Glen Muick and Cromar areas are characterised by a considerable amount of retrogressive metamorphism. This consists of the results of regional retrogression and of much later contact metamorphism. It is a considerable problem to distinguish the two. First a brief description of undoubted hornfelses will be given and then the retrogression of rocks of more uncertain origin will be described.

3.4.1 Hornfelses

Two general types of hornfels might be considered to be present. Descriptions have been given by Chinner (1962) and Ashworth and Chinner (1978). The first is associated with Newer Diorite contacts and comprises the metapelite maximum assemblage garnet-orthopyroxene-cordierite-plagioclase-quartz-K feldspar opaques. Sillimanite occurs as fibrolite not as prismatic sillimanite and does not coexist with garnet. It generally occurs in areas with the assemblage cordierite-plagioclase-Kfeldspar-spinel-corundum. Garnet, orthopyroxene and cordierite are all equigranular and fine grained and for the most part in good textural equilibrium. Muscovite is absent from these hornfelses, although this of course may not be so further away from the diorite.

In cooler Newer Granite aureoles hornfelses apparently never contain orthopyroxene or garnet and usually not sillimanite. Andalusite is the stable aluminosilicate polymorph. These rocks are relatively fine grained and for the most part in good textural equilibrium. The maximum assemblage is cordierite-K feldspar-biotite-plagioclase-andalusite-quartz-opaques. Small retrogressive muscovites may occur. The andalusite may occur as small aggregates or as large porphyroblasts.

In the Pollagach Burn (N0407943) Newer Granite contact metamorphosed limestones occur. These spectacular rocks contain the assemblage garnet-wollastonite-plagioclase-diopside-vesuvianite-opaques.

Further away from the granites incipient effects of contact alteration include:

- (1) reaction rims of cordierite between regional sillimanite and biotite.
- (2) cordierite replacing garnet (see figure 3.20).
- (3) development of foxy red hornfelsic biotite.

Often in rocks in which cordierite is extensively developed the regional biotite fabric is retained. Not all contact metamorphic affected rocks show clear new biotite. These textures can be reasonably confidently assigned to contact alteration. Now textures and assemblages will be discussed of more equivocal origin.

3.4.2 Retrogressive Metamorphism

Garnets are generally irregularly shaped in Glen Muick metapelites even in otherwise texturally fresh rocks. They are not euhedral. In AB430A they are non euhedral and surrounded by feldspars and quartz (figure 3.9). In more deformed rocks they are embayed and often elongate within the foliation. In other instances the garnets are replaced by large decussate biotites of apparent regional origin. In the most retrogressed rocks the garnets are extensively fractured and resorbed. Along the fractures they are replaced by fine muscovites and biotites. Other modes of garnet replacement include replacement by chlorite, by cordierite in some hornfelses, or by plagioclase. It can be observed that much of this late stage garnet replacement is post deformational. Fragmented garnets have not been deformed.

3.4.3 Staurolite bearing assemblages

Some high grade gneisses contain staurolite. It is established that peak metamorphic regional staurolite occurs to the west in Glen Gironck

and to the south in the low sillimanite zone. Staurolite in the high grade gneisses is of retrogressive origin, of regional or contact metamorphic origin or both.

One example (AB938A) (figure 4.11a) from a coarse gneiss to the west of Glen Muick contains large staurolite porphyroblasts. The assemblage is muscovite-biotite-plagioclase-quartz-staurolite-sillimanite-chlorite-opaques. The rock is a deformed pelitic migmatitic gneiss. It is retrogressed with chloritised biotite and crosscutting muscovites overgrowing fibrolite trails orientated parallel to the foliation. Sillimanite also occurs as small aggregates of fine prismatic crystals. Some of these aggregates are overgrown by later staurolite porphyroblasts, which were in turn later surrounded by small rims of shimmer aggregate. This retrogressed assemblage is apparently comparable with staurolite-biotite-muscovite-quartz assemblages to the immediate west in Glen Girnock. It is presumed to be of regional origin.

Just east of the Coyles of Muick (AB415 and AB922A) staurolite occurs as small grains in and near garnet. In AB922A staurolite occurs inside the garnets and immediately adjacent to them. The staurolites are associated with shimmer aggregate and green hercynite overgrowths on earlier magnetites. The staurolites included within garnets are interpreted as retrogressive on account of their association with other retrogressive features e.g. the shimmer aggregate. The garnets are well fractured permitting the growth of new phases within the garnet. The rest of the rock could be said to be texturally fresh with the assemblage garnet-plagioclase-quartz-biotite. Similar staurolites occur as retrogressive "inclusions" within garnet in AB415.

In E Glen Muick staurolite occurs in the centres of garnets replaced by much biotite in AB560A. These rocks are considerably retrogressed and contain large amounts of andalusite and fibrolite.

The other occurrence of staurolite is from the hill of Craig Ferrar on Deeside where staurolite occurs in andalusite bearing rocks described in the next chapter (see also figure 3.17).

The origin of this staurolite is uncertain. Staurolite in contact metamorphic rocks of the area is normally replaced by cordierite. In Glen Gironck staurolites are replaced by reaction rims of cordierite. This would suggest that the late staurolite in the area is of late regional origin. However in AB560A and in some Craig Ferrar rocks it is associated with cordierite. The stability of staurolite-spinel assemblages is illustrated for the system KFLASH in figure 3.18 after Richardson (1968). Allowing for the multivariance of the reactions involved the staurolite could be of contact metamorphic origin. The assemblage reflects pressures of about 3kb. It is also appropriate to note that retrogressive staurolite is known from other Dalradian migmatites (Chinner, 1961; Ashworth, 1975).

3.4.4 Andalusite Bearing Rocks

In Glen Muick and Cromar a number of rocks outside of Newer Granite aureoles are andalusite bearing. East of Hare Cairn andalusite occurs in muscovite-biotite rocks. Around Drum Cholzie andalusite occurs overgrowing fibrolite in aluminosilicate rich rocks. These are very retrogressed. Garnet is very fragmented and resorbed and some cordierite is developed. These occurrences are discussed in more detail in the next chapter.

Muscovite

Muscovite occurs in a variety of forms. It may occur as large randomly orientated porphyroblastic muscovites in migmatized metapelites. Shimmer aggregate is often found around sillimanites or sillimanite aggregates or replacing feldspars. In the Glen Tanar-Hare Cairn area muscovites lie within the foliation, some being strained. Fine muscovites in shimmer aggregate are parallel orientated (figures 3.11, 3.20 & 4.12).

In some of these rocks chlorite is also developed. It lies within the foliation and also replaces garnet. It is possible that some of this chlorite is replacive of biotite. The retrogressive growth of muscovite and chlorite in this area seems to have been late regional in that the growth is associated with a penetrative phase of regional deformation. Also associated with this retrogression are some andalusites.

A number of mica rich rocks occur (e.g. 454, CF etc.) composed dominantly of large decussate muscovites and biotites with more minor quartz, plagioclase and often sillimanite. The micas form large randomly orientated porphyroblasts, riddled with opaques. Chlorite pools also occur. Some are andalusite bearing and in the case of those from Cromar also contain staurolite.

Many retrogressed rocks contain large amounts of fibrolite as opposed to single sillimanites and aggregates of prismatic sillimanite. The fibrolite may itself be a retrogressive feature.

The distinction between regional retrogression and contact alteration remains a problem. Uplift after the regional event and later contact metamorphism might be expected to produce similar assemblages and textures.

3.5 MINERAL ZONES

Mineral zones are illustrated in figure 3.21. The assemblage sillimanite-K feldspar is recorded from Cairn Leuchan, Cromar, SW Glen Muick, but not from areas to the SE. Muscovite is not present in these assemblages as a product of peak metamorphism. Most sections do not show the coexistence of sillimanite and K feldspar and are trondjhemitic. Sillimanite-K feldspar may also occur in the Duchray Hill Gneiss (E. McLellan, pers. comm.). The regional extent of the regional sillimanite-K feldspar zone is uncertain. The assemblage has been demonstrated for some rocks in Cromar. However its eastern extent is obscured by lack of study

of the area concerned, poor outcrop and by overprinting due to later retrogression. The Cromar area would formerly have been considered to have equilibrated at lower grade than indicated by the preservation of high pressure relics. Muscovite is absent from metapelites except as a retrogressive product.

Glen Girnock lies within the kyanite zone transitional to the sillimanite zone as indicated by a few sparse shreds of fibrolite. The extent of andalusite and kyanite zones at various times in this area is discussed in chapter 3. An andalusite zone may have existed at a late stage along Deeside, but if it is early it must occur further to the north.

It is hard to define the muscovite out isograd precisely as

- (1) exposure is very poor in the area of the isograd.
- (2) there is much retrogressive muscovite in rocks to the north.

However rocks in Glen Mark appear to contain muscovite in equilibrium with the other phases. To the north this is not so. Muscovite is believed to be present only in retrogressed assemblages. Therefore the muscovite out isograd lies somewhere a little way to the north of Glen Mark. It is difficult to determine the extent of the sillimanite-K feldspar zone as muscovite disappears from metapelites before the occurrence of sillimanite K feldspar assemblages.

A garnet-clinopyroxene-quartz zone may be defined in metabasites. The garnet-cpx-qtz in isograd lies to the north of Glens Clova and Mark. The garnet-cpx-qtz zone includes the northeastern corner of the Duchray Hill Gneiss. It lies above the sillimanite isograd. A similar zone based on the appearance of this assemblage in metabasites has been reported by Ghent et al. (1983), from another terrain.

It is clear that there is metamorphic continuity along strike between Cromar, Glen Muick and the Duchray Hill Gneiss as evidenced by the

occurrence of (garnet)-cpx-qtz and sillimanite-K feldspar assemblages from all these areas. This metamorphism is inferred to be all of the same age and therefore presumably of Grampian origin.

3.6 VARIATIONS IN PRESSURE AND TEMPERATURE

P-T determinations for the area are shown in figures 3.22 through 3.24 and are derived from the methods described in chapter 6.

Geothermobarometrical estimates for Glen Muick from metabasites and metapelites indicate that very high pressures and temperatures were reached. Temperatures are estimated from various exchange thermometers. These temperatures are tentatively supported by experimental evidence for the first appearance of clinopyroxene in metatholeites at circa 750°C (Spear, 1981). Pressures of about 8kb at 800°C are estimated from (chapter 4):

(1) ALSIL

(2) CPX

(3) The whole rock experiments of Green and Ringwood (1967).

Temperatures and pressures of similar magnitude are also estimated from Cromar to the north. To the south there appears to be a uniform increase of temperature from Glens Esk and Clova as indicated by garnet biotite and garnet amphibole thermometry.

In Glen Girnock garnet biotite temperatures indicate about 650°C to 680°C supported by the coexistence of staurolite with very magnesium poor biotite. Temperatures are limited to a maximum of about 680°C by the maximum stability of staurolite+quartz (Rao and Johannes, 1979). If these rocks equilibrated somewhere near the kyanite-sillimanite equilibrium as evidenced by kyanite coexisting with sporadic fibrolite then pressures of about 7kb are indicated.

There is a strong contrast in grade between the rocks of Glen Girnock and those of Glen Muick. Temperatures increase gradually towards the

sillimanite-K feldspar zone in Glen Muick and the decrease suddenly to Glen Girnock. Temperatures of about 680°C in Glen Girnock compare with about 800°C in Glen Muick. In Glen Muick metabasites contain garnet-clinopyroxene and metapelites, sillimanite-K feldspar. Muscovite only occurs as a retrogressive mineral. In Glen Girnock metapelites contain kyanite-staurolite-muscovite with only very occasional sparse fibrolite. Metabasites never contain garnet or clinopyroxene and there is no evidence for migmatisation in any lithology. Primary muscovite occurs in a coarse schistosity intergrown with biotite. There is no intervening alsilicate zone with staurolite absent. This rapid transition in grade coincides with a band of metagabbro and serpentinite. Garnet-clinopyroxene and muscovite absent sillimanite bearing assemblages occur to the east and kyanite-staurolite-muscovite assemblages to the immediate west. This abrupt thermal transition is attributed to a structural break.

On the western end of Craig Megen (NW of N0317895) apparently low grade amphibolites are interbanded with coarse sillimanite gneisses, affected by contact metamorphism. Kyanite staurolite schists occur to the west around (N0306924). Around The Coyles of Muick garnet clinopyroxene amphibolites occur close to the east of the serpentinite (858) and sillimanite bearing gneisses to the immediate east (924). To the immediate west of the serpentinite and metagabbro kyanite-staurolite-biotite muscovite schists occur (535 & 468). To the north (around N0331935) two amphibolite bands are present. Retrogressed migmatitic gneisses occur to the east. Unmigmatized metapelitic schists occur to the immediate west of the eastern band. One rock here contains prismatic sillimanite, overprinted by muscovite and staurolite (938A). Most rocks are staurolite schists with a well developed muscovite schistosity.

3.7 STRUCTURE

The Glen Muick area lies in a zone of steeply dipping foliation and bedding. In the Cromar area to the northwest the dip of the foliation become shallower and rather variable. To the southeast the dips of the foliation and the stratigraphy shallow out to become subhorizontal in Glens Esk and Glen Clova. Glen Clova lies in the lower inverted limb of the SE facing Tay Nappe. It is suggested by Harte (1979) that Glen Esk lies in a structurally lower Tarfside Nappe and that the stratigraphy is there right way up (figure 3.25). In Glen Girnock the foliation dips steeply to the southeast, but shallows towards the west.

Glen Muick lies in a steep belt which marks the northern limit of the flat belt of the Tay Nappe. A similar steep belt is described by Bradbury et al. (1979) from the northern margin of the flat belt to the southwest. This is the Tummel Steep Belt. The steep belt in Glen Muick is probably an analogous structure.

The dominant steep foliation lies axial planar to isoclinal to tight decimetre scale folds (D_2^m) with subvertical axial planes and NE-SW trending axes of variable plunge. Commonly the axes are steeply plunging. To the SE in Glen Mark the last major phase of folding has axes of similar trend, but with more flat lying axial planes (Harte and Johnson, 1969). Earlier deformations there have axes which trend NW-SE.

Locally in Glen Muick these folds are deformed by later decimetre to metre scale folds of monoclinial form with NW dipping axial planes (D_3^m) (figure 3.26). These folds do not generally produce an axial planar foliation except very locally. It is possible to distinguish occasional folds (D_1^m) which predate the upright folds. The D_2^m upright folds also

deform a compositional foliation and mica fabric indicating the occurrence of earlier "phases" of deformation. There are also some late brittle folds of only local importance.

On the east side of Glen Muick there appears to be a belt where the deformation begins to become more intense. In quartzites and migmatitic gneisses the fabric developed appears to be more intense compared with that to the west. These fabrics continue in rocks in Glen Mark to the southeast. In some areas strongly sheared fabrics are developed, for instance around N0389928 where a band of steeply dipping strongly sheared quartzites several metres wide is developed.

Glen Girnock is characterised by steeply plunging linear structures. In more competent lithologies such as psammitic schists folds have axes which plunge very steeply towards the southeast producing a deformation of intense linear aspect D_2^g . This lineation is parallel to one defined by hornblendes in amphibolites and a quartz rodding lineation in metapelitic rocks. This quartz rodding lineation represents quartz localised in the hinges of folds. The folds are now only sometimes discernable on account of occasional fold closures and "hooks". Whereas this deformation has produced open folds in psammitic lithologies the less competent metapelites have been isoclinally folded and traces of the folding essentially removed. Later crenulations (D_3^g) of subhorizontal aspect are occasionally present.

3.7.1 Structural Correlations

Precise regional correlations of deformation phases for rocks in this area will not be suggested as I believe, as explained in the introduction, that such correlations are fraught with difficulties.

Late D_3^m monoclinial folds in Glen Muick are probably comparable with

similar folds to the SE in Glen Esk (local D4:Harte and Johnson,1969). Earlier phases of folding observed by Harte and Johnson (1969) in Glen Esk comprise:

D3: NE-SW axes

D2: NW-SE axes

One might propose the correlation of Glen Muick D_2^m folds with either of these local fold phases to the south. It might be expected that fold axes would change orientation from NE-SW to NW-SE with the progressive translation of the folds by shear within the Tay Nappe (see Roberts and Sanderson,1974). Thus one might imagine that Glen Esk D2 corresponds to rotated Glen Muick D_2^m or alternatively Glen Esk D3 with unrotated Glen Muick D_2^m . Correlation of fold episodes between Glens Muick and Glen Girnock is uncertain. The steep lineation in Glen Girnock is of consistently steep orientation while fold axes in Glen Muick have a very variable dip. It might be suggested that the two are contemporaneous. No refolding relationships have been found.

The zone of steeply dipping fold axes in Glen Girnock may be comparable with a number of other Dalradian zones where intense deformation has rotated fold axes into the extension direction (Coward,1983a; Shackelton and Ries,1984). If so this zone would have resulted from NW directed sliding and emplacement of the sillimanite zone on to more north westerly rocks.

The significance of the steep belt is uncertain. It is interpreted by Bradbury et al. (1979) as a late rotation zone about which the Tay Nappe was translated to the south. To the SE of Glen Muick structures flatten out. Deformation here presumably reflects translation of the Tay Nappe to the south (see Bradbury et al.,1979). In Glen Girnock the steeply dipping lineation may reflect translation to the NW. The change in vergence across

the steep belt is not interpreted as primary. By analogy with deformation schemes to the southwest it seems reasonable to assume that the SE directed movements preceded those to the northwest.

3.8 STRUCTURAL-METAMORPHIC RELATIONSHIPS

The relationships of the various thermal events will now be discussed with respect to different deformational episodes.

3.8.1 Glen Muick

Migmatisation

Migmatitic leucosomes which are believed to represent partial melts carry variable fabrics. In many areas the fabrics are indistinct or absent while in other areas a more intense fabric is evident. Fabrics may be defined by a quartz-feldspar shape alignment or an alignment of sparse biotite within the leucosome. These fabrics where present are axial planar to the last major phase of folding D_2^m in Glen Muick and Glen Mark. This indicates that migmatisation preceded the last major phase of deformation.

Leucosomes generally seem to carry stronger fabrics to the east of Glen Muick. To the west it is often impossible to discern any fabric. This might reflect one of two alternatives.

- (1) deformation was more intense in the east. In the west it was not sufficient to impose strong fabrics on the leucosomes.
- (2) deformation was later in the east than in the west.

It is assumed that it is reasonable to treat migmatisation as coeval over the study area implying a greater intensity of deformation in the east.

Sillimanite

The mode of occurrence of sillimanite in this area is discussed in chapter 4. A number of criteria indicate that sillimanite predated the last major deformation. Prismatic sillimanites nearly always lie within

the foliation and are sometimes deformed around garnet. Aggregates of prismatic sillimanite lie within the foliation and are sometimes axial planar to D_2^m folds (figure 3.27). The sillimanite aggregates are kinked by the late monoclinial folding (figure 3.28). Sillimanite predated the last major phase of deformation and the still later monoclinial folding.

Feldspars

As stated above some migmatitic leucosomes are undeformed. In deformed examples K feldspars and plagioclases are augened within the foliation.

Garnet

Metapelite garnets do not usually have euhedral outlines. They are variably resorbed and fractured. Often they are elongate within the foliation indicating that their growth predated the last penetrative phase of deformation.

Muscovite

Muscovite occurs as large randomly orientated porphyroblasts or as shimmer aggregate. Growth of both these forms occurred post deformationally. In the southeast towards Hare Cairn and Glen Tanar some fine muscovite does lie within the foliation. It is concluded that most muscovite is post deformational.

3.8.2 Glen Girnock

The textural relationships of porphyroblasts in Glen Girnock are difficult to establish as they are commonly replaced by shimmer aggregate, contact metamorphic biotite or cordierite.

In poly deformed terrains porphyroblast matrix relationships should strictly be established in fold hinges where one can be certain of the age of the mica fabric in question. Earlier mica fabrics may persist outside the fold hinges (Harte and Johnson, 1969). In Glen Girnock metapelites

have undergone such intense deformation that fold closures are often not preserved. They are only sometimes visible in quartz segregations. In most thin sections muscovite-biotite form a relatively coarse schistosity. This is occasionally crenulated by the late phase of subhorizontal crenulation. In some cases it is possible to discern the original presence of isoclinal folds. The hinges no longer exist and have been replaced by new axial planar mica.

The relationship of the D_2^g schistosity to porphyroblast phases will now be considered. Kyanite is aligned within the schistosity. It is not kinked. Sometimes it is embayed and surrounded by coarse muscovite with some rare included swirls of fibrolite. Elongate staurolites are aligned within the schistosity. Where quartz inclusion trails are present within the staurolite or garnet they may be rotated or straight and generally not continuous with the external schistosity. Strain shadows are sometimes present around porphyroblasts. In other instances garnets, staurolites or kyanites appear to overgrow the muscovite biotite schistosity without it being deformed around them.

It is concluded that the porphyroblasts grew during the imposition of the D deformation. This is supported by the occurrence of a hornblende lineation paralleling the fold axes of this generation indicating that hornblende grew at this stage.

There are indications from 938A that staurolite growth in Glen Girnock postdated sillimanite growth in Glen Muick. This rock contains staurolite overprinting earlier prismatic sillimanite aggregates. The rock occurs from between amphibolite bands to the immediate west of the serpentinite.

CONCLUSIONS

Stratigraphy is continuous between rocks within the Tay Nappe and those within the basal gneiss unit of the Banff nappe (as described by Ramsay and Sturt, 1979). There is no structural, metamorphic or stratigraphic break perpendicular to strike. It is concluded that since

stratigraphic units to the southwest are of undoubted Dalradian age that there is no Pre-Cambrian basement slice in NE Scotland.

Very high grade rocks are found in Glen Muick transitional to the granulite facies. Migmatized metapelitic gneisses contain sillimanite-K feldspar and migmatized metabasites contain garnet-clinopyroxene. These high grade rocks are separated from lower grade kyanite-staurolite-muscovite schists to the west by a belt of serpentinite and metagabbro. There is a sharp thermal transition between these different grades. A regional garnet-clinopyroxene zone may be mapped in metabasites.

P-T conditions are estimated using the methods of chapter 4 at 8kb and 800°C for rocks in Glen Muick and Cromar. These pressures and temperatures are considerably higher than hitherto assumed and are inconsistent with the simultaneous presence of andalusite.

The Glen Muick area lies in a steep belt which marks the northern limit of the flat belt of the Tay Nappe. It comprises a fan of planar and linear structures across which vergence changes which is probably an analogue of the Tummel Steep Belt to the southwest. To the west in Glen Gironck fold axes dip steeply parallel to a strong lineation. This may represent a zone of NW sliding.

Migmatization and sillimanite growth predated the last major phase of folding in Glen Muick. This contrasts with sillimanite later than the last major phase of deformation to the south.

Retrogression is extensively developed in Glen Muick rocks. Part is of regional and part of contact metamorphic origin. Separation of the two is fraught with difficulty. Extensive fluid movement must have occurred through these rocks either during uplift after the metamorphic peak or during the intrusion of the Newer Granites. If the retrogression is related predominately to Newer Granite contact effects it may be widespread over much of NE Scotland.

CHAPTER 4

ALUMINOSILICATE POLYMORPH RELATIONSHIPS

In this chapter the relationships between the aluminosilicate polymorphs will be described and the implications discussed for the regional evolution. In the west (Portsoy to Braemar) the andalusite zone is separated from the kyanite zone by an apparently well defined isograd (Chinner and Heseltine, 1979). To the south and east a sillimanite zone exists between kyanite and andalusite zones, within which andalusite or kyanite often coexist with sillimanite (see figure 4.1). Sillimanite occurs as fibrolite at the lower grades and as prismatic sillimanite at higher grades. Within the sillimanite zone separation of regional andalusite from later contact metamorphic andalusite is often a problem, as large bodies of Newer Granite intrude much of the area. Chinner and Heseltine (1979) have attempted this separation.

The fact that sillimanite often coexists with another aluminosilicate polymorph led to the suggestion that the sillimanite was a separate later overprint, on previously existing kyanite and andalusite zones. This overprint was hypothesised to have arisen from a later isobaric temperature rise (Chinner, 1966). More recently the overprint has been suggested to be of a more progressive nature (Harte and Hudson, 1979; Chinner, 1980). A contrasting hypothesis derived from thermal modelling suggests that sillimanite was developed more by near isothermal uplift than by isobaric temperature rise (Wells, 1979). Locations mentioned in the text are detailed in figure 4.2. Further data on aluminosilicate bearing rocks is included in the appendices.

4.1 Glen Muick

Sillimanite in the sillimanite- K feldspar zone in Glen Muick occurs commonly as :

- (1) discrete prismatic sillimanites.
- (2) aggregates of fine prismatic sillimanite which may be parallel orientated (figure 4.3).

(3) fibrolite mats.

Sillimanite may occur as a combination of any of these forms within any one thin section. Fresh unretrogressed, poorly foliated sillimanite-K feldspar gneiss (430A) (figure 3.10a) contains only discrete prismatic sillimanites. These occur associated with biotite garnet rich areas while the rest of the rock is composed dominantly of quartz and feldspar. In compositionally banded migmatitic gneiss sillimanite may also occur as large discrete prisms up to about 1cm long, often associated with some other form of sillimanite.

Commonly the sillimanite occurs as aggregates composed exclusively of prismatic sillimanite. These are often very fine, parallel orientated prismatic sillimanites. In some instances these appear as a fine mosaic of diamond shaped cross sections. The aggregates are often associated with larger individual prismatic sillimanites. They commonly have dimensions of about 5-10x2x1mm, which would be compatible with pseudomorphism after kyanite. It is possible that the aggregates may arise from deformation of larger sillimanites or the larger sillimanites from recrystallisation of the aggregates. Sometimes individual sillimanites within aggregates of parallel orientated sillimanite have the appearance of being subgrains of a larger sillimanite.

Fibrolite mats appear in many rocks. Fibrolite may grow on biotite in the manner described by Chinner (1961) so that eventually only a few relict biotites remain within the mat enveloped in swirls of fibrolite. Often fibrolite mats are not associated with biotite. Fibrolite occasionally occurs as swirls in late muscovite. They may be of random complexly folded form or comprise straight inclusion trails continuous with trails in muscovites of differing orientation. These trails are parallel with the external fabric in the rock. Often it appears that fibrolite occurs in rocks that have been subject to retrogression, while

fresher rocks seem to contain coarser grained sillimanite, with fibrolite absent.

Occurrences of distinctive aggregates of randomly orientated prismatic sillimanite have been found in one area to the southeast of Glen Muick (AB563 GR N0385884, see figures 4.4 and 4.7). These appear to be pseudomorphous after some other mineral. This is concluded to be kyanite on account of the bladed habit (dimensions ~50mmx5mmx5mm) of the pseudomorphs and the proximity of the kyanite-sillimanite isograd to the south. These aggregates are now surrounded by "coronas" of shimmer aggregate. The rest of the rock is composed of coarse decussate muscovites and biotites. Andalusite also occurs in the rock (see below).

The origin of the smaller sillimanite aggregates of non bladed form is uncertain. They are more irregular and are less obviously pseudomorphs. It is possible that they are pseudomorphous after kyanite. However other origins should be considered. Aggregates might form from deformation of larger sillimanites. Similar shaped fibrolite mats sometimes arise from growth of fibrolite on biotite. Later partial recrystallisation and grain growth might occur to produce the observed aggregates. While it is possible that some of these smaller aggregates might be after kyanite, this is by no means certain and other origins are possible.

Andalusite in Glen Muick

Andalusite occurs at a number of localities in Glen Muick that are not obviously associated with Newer Granite contact metamorphic aureoles. It normally occurs as coarse randomly orientated porphyroblasts in rocks which are variably retrogressed. In these retrogressed rocks garnets are fractured and resorbed and fibrolite, shimmer aggregate and chlorite are often found.

Andalusite often overgrows fibrolite mats and trails. Fibrolite mats are deformed around garnet and later overgrown by andalusite (figure

4.5). Sometimes small fractured garnets are included within andalusites. In one instance (AB560, N0349888) an embayed aggregate of prismatic sillimanite is partially included in andalusite. Trails of orientated fibrolites are included within andalusites, as are crenulated mats of fibrolite (figure 4.6). Andalusites are generally well formed and unresorbed while garnets are extensively replaced by biotite and shimmer aggregate. The textures clearly indicate that andalusite is later than fibrolite. A number of individual occurrences are worthy of comment:

(1) Glen Tanar 1: AB563 N0385884:

Well formed andalusites occur within a rock composed dominantly of large decussate muscovites and biotites, quartz, plagioclase and shimmer aggregate. Polycrystalline aggregates of sillimanite probably pseudomorphous after kyanite occur as described above. These aggregates of sillimanite are surrounded by rims of shimmer aggregate. Randomly orientated andalusites overprint the sillimanite aggregate and corona of shimmer aggregate (figure 4.7).

(2) Glen Tanar 2. AB454 N0385886:

Andalusite occurs in a sheared gneiss in which extensive shimmer aggregate and muscovite occur. Fine micas in the shimmer aggregate and coarser muscovites are orientated parallel to the fabric in the rock. An andalusite porphyroblast occurs and lies within the foliation (figure 4.12).

(3) East Glen Muick AB560 N0349888:

Andalusites occur within a relatively undeformed gneiss that is strongly retrogressed. This andalusite overprints and overgrows mats of fibrolitic sillimanite. New biotite has grown around the margin of the andalusite. Garnets are fractured and replaced by aggregates of white mica and biotite with occasional staurolite. Some cordierite occurs. These andalusites may be the result of contact metamorphism.

The evidence described above indicates that all the andalusite in Glen Muick is later than sillimanite growth and than the peak metamorphism. The evidence for this may be summarised:

(1) it occurs in retrogressed rocks while the andalusites themselves are texturally fresh.

(2) it overgrows orientated trails of fibrolite.

(3) it includes resorbed garnets and resorbed aggregates of prismatic sillimanite.

Its origin, regional retrogressive or much later contact metamorphic remains to be established.

4.2 Glen Girnock

In Glen Girnock to the west of Glen Muick three examples of regional aluminosilicate mineral have been found. They are all kyanite. They lie within the foliation and are surrounded by moderately coarse muscovites which include sparse fibrolite swirls. This confirms that the area lies effectively within the kyanite zone as originally suggested by Barrow (1893). The amount of fibrolitic sillimanite developed is very small (see figure 3.16).

4.3 Lochnagar Granite Aureole

Along the southern margin of the Lochnagar Granite Chinner and Heseltine (1979) find aggregates of contact metamorphic andalusite presumed to be pseudomorphous after kyanite. This is apparently not so along the northern margin. In figure 4.8 an aggregate of three andalusites from the northern margin (W side of Leac Grom N02394) is shown, the shape of which is suggestive of pseudomorphism after kyanite. The kyanite zone appears to extend further to the north on the evidence of several kyanites in Glen Girnock metapelites. Kyanite may once have been stable in rocks presently to the north of the Lochnagar intrusion.

4.4 South of Glen Muick

Textures involving sillimanite in the area to the south of Glen Muick have been described by Chinner (1961) and Harte and Johnson (1969). Sillimanite has only been found in the fibrolitic form e.g. as intrafolial mats, veinlets, growths on biotite or as swirls within muscovite. Sillimanite bearing rocks have been collected from the area immediately to the south of Glen Muick.

In the Glen Mark area (between Glens Muick and Esk) no coarse prismatic sillimanite or kyanite bearing rocks have been found. Many of the pelitic compositions do however contain fibrolitic sillimanite. Sillimanite may occur as fine isolated needles, small mats of fibrolite or fibrolite included within muscovite.

In AB867 (N0363852) areas of shimmer aggregate and slightly coarser muscovite are found. Fibrolite is associated with some of these areas. In AB955A (NN366854) fibrolite overgrows schistosity biotites in the manner described by Chinner (1961) eventually producing great swathes of fibrolite.

Some rocks in the area (827A, N0385837 and other migmatized metapelites in the upper part of Glen Mark) contain pseudomorphs several centimetres long now composed essentially of muscovite. These are very similar in shape to the prismatic sillimanite aggregate pseudomorphs described from the Glen Tanar area to the north. They are composed either of fine shimmer aggregate or of relatively coarse muscovite. One example is composed of very large muscovites, orientated randomly compared with the orientated muscovites outside the pseudomorph. Later kink and shear bands are developed within it (figure 4.9). Fibrolite occurs within the pseudomorphs. Fibrolite trails are orientated parallel to the length of the pseudomorph and parallel to the external schistosity in the rock. Where pseudomorphs are composed of many randomly orientated muscovite

porphyroblasts the fibrolite trails are continuous between adjacent muscovites of variable orientation. Such a situation is illustrated in figure 4.10 for rocks from Glen Clova and Glen Muick. These pseudomorphs are interpreted as being pseudomorphous after kyanite on account of:

- (1) their dimensions
- (2) proximity to the kyanite sillimanite isograd
- (3) partial replacement of kyanite by muscovite is very common further to the south.

To the south of the Mark-Muick area direct evidence for the relationships between kyanite and sillimanite is not abundant. There are virtually no examples of direct replacive relationships (see Harte and Johnson, 1969). Generally evidence is limited to embayed kyanite surrounded by muscovite, in which sparse fibrolite strands and swirls are found. It is appropriate to note at this stage the evidence for late kyanite and staurolite, which postdate fibrolite on Ben Reid in Glen Clova (Chinner, 1961). In examples collected by the author relatively large staurolites overgrow and include continuous fibrolite trails (figure 4.11b). Staurolite later than sillimanite has also been found from west Glen Muick (figure 4.11a). Kyanite, predating and postdating sillimanite growth in Glen Clova (Chinner, 1961) may reflect a pressure temperature path subparallel to the kyanite-sillimanite equilibrium.

4.5 Cromar

This area lies to the north of Chinner and Heseltines andalusite-kyanite isograd. The maximum grade reached is that of the sillimanite-K feldspar zone. In relatively fresh sillimanite-K feldspar gneisses sillimanite occurs in a number of forms. Commonest is its occurrence as relatively coarse isolated prisms orientated within the foliation. Fibrolite is in these cases absent. In other instances the fabric within the rock is weaker and the prismatic sillimanites are more randomly

orientated. Prismatic sillimanite commonly occurs as aggregates, together with minor biotite and ilmenite. These aggregates are often wrapped around garnets. In these aggregates there may also be fibrolite mats and bundles of parallel orientated prismatic sillimanite. They may arise as a result of deformation of larger monocrystalline sillimanites. Concentrations of sillimanite in such aggregates may be a result of original growth of fibrolite on biotite near garnet (Yardley, 1979) followed by later recrystallisation to produce prismatic sillimanite. There is no evidence for pseudomorphism after either kyanite or andalusite. The aggregates do not appear to be regularly shaped.

Andalusite bearing rocks

Andalusites occur in various pelitic migmatites in Cromar. They are found as large porphyroblasts in retrogressed muscovite-biotite rich melanosomes in stromatic migmatites where they commonly include staurolite and in non stromatic gneisses where they replace aggregates of sillimanite (figures 4.12 and 4.13).

In the gneisses aggregates of sillimanite are replaced by shimmer aggregate and associated fibrolite. Andalusites overgrow the shimmer aggregate and contain trails of fibrolite. They may also include prismatic sillimanites. In 919B (south of Scar Hill, Cromar) prismatic sillimanites are included within andalusite and also exist outside. The sillimanite appears to show some signs of embayment. In another instance (DH4, Dinnet House, Cromar N0451979) andalusites overgrow resorbed and fragmented garnets indicating that they are clearly not part of the peak metamorphic garnet-sillimanite-K feldspar assemblage (figure 4.5).

On the hill of Craig Ferrar retrogression is more extensive. The rocks concerned are pelitic migmatites. Melanosomes are composed of muscovite-biotite-fibrolite-andalusite-staurolite-chlorite-quartz-plagioclase-garnet with occasionally cordierite. Shimmer aggregate is

abundant. Most of the rocks consist of large decussate muscovites and biotites. These are sometimes partially orientated. Trails of opaques occur due to exsolution from biotite. Chlorites also occur as crosscutting pools. Andalusites overgrow muscovites and biotites and include orientated trails of fibrolite. Andalusites and staurolites overgrow the trails of opaques. Andalusites sometimes include staurolites. Shimmer aggregate and fine micas surround the andalusites. These textures are interpreted as indicating that andalusite is late, as in Glen Muick.

4.6 Andalusite and Sillimanite elsewhere

Maryculter

Andalusite bearing rocks have been collected from Maryculter (N0852994), further to the east along Deeside. The occurrence is texturally similar to that on the hill of Craig Ferrar.

MC5 (figures 4.15 and 4.16) contains fibrolitic sillimanite, biotite, coarse porphyroblastic muscovite, much shimmer aggregate and finer randomly orientated muscovite. Opaques are concentrated in and around large biotites while they are absent from fibrolite mats. Fibrolite trails are often aligned within porphyroblastic muscovites. Sometimes trails between different muscovites and quartz are continuous. In other instances the fibrolite forms irregular swirls. The trails of fibrolite tend to be parallel to the external fabric in the rock although the including minerals may be randomly orientated. Some areas of the rock are occupied by fibrolite mats rimmed by shimmer aggregate and in turn surrounded by large biotites associated with opaques. By analogy with textures in the Cromar rocks they are interpreted as former aggregates of prismatic sillimanite.

MC4 contains large randomly orientated andalusites which include opaques exsolved from biotites, fine muscovites and biotites and fibrolite. Biotites and large porphyroblastic muscovites are randomly

orientated around the andalusites. Semi continuous fibrolite trails are visible within the andalusites. It is possible to distinguish areas within andalusites formerly occupied by fibrolite mats and by biotites. The former are full of strands of fibrolite and the latter with opaques exsolved from biotite (figure 4.16). Andalusite is late because:

- (1) it includes orientated fibrolite trails.
- (2) it includes randomly orientated muscovites and biotites.
- (3) it includes opaques exsolved from biotites during retrogression.
- (4) it is possible to identify areas within the andalusites formerly occupied by aggregates of sillimanite and by micas.

This occurrence is moderately close to a Newer Granite. Again it is uncertain whether retrogression might be attributable to regional or to contact metamorphic effects.

Other Areas

Donside

A small number of rocks collected from this area contain both andalusite and sillimanite. AB599 (NJ506154) and AB600 (NJ482150) contain andalusite being replaced by aggregates of large porphyroblastic muscovite. Andalusite is only sometimes preserved within the centre of the muscovite aggregates. Muscovite is absent from the rest of the rock. Biotite throughout the rock is overgrown by fibrolite mats. This may reflect the progress of the reaction andalusite \rightarrow fibrolite by a Carmichael (1969) type mechanism, although it would appear that the reaction requires metasomatism on a scale greater than that of the thin section. Alternatively, this may reflect replacement of the andalusite at some stage after the development of fibrolite (Kwak, 1971). However the fibrolite does appear to be concentrated around the muscovite replacing andalusite. The textures are tentatively interpreted as indicating the progress of the reaction andalusite \rightarrow fibrolite.

Newer Gabbro Aureoles

In some Newer Gabbro aureoles there is evidence for the reaction :



Prismatic sillimanite occurs as coarse aggregates of perfect square form without any additional minor phases (figure 4.18). They have been found within the aureole of the Haddo House Gabbro (NJ482150, rock 606) and also the aureoles of some other gabbros (G. Droop, pers. comm.).

Ashworth (1975) suggests that the reaction



occurred in the Cowhythe Gneiss, on the evidence of andalusite replaced by muscovite, accompanied by fibrolite within the sillimanite zone (c.f. Kwak, 1971).

Stonehaven Coast

Booth (1984) reports fibrolitic sillimanite from the Stonehaven Coast Section where it replaces staurolite of apparently the same generation as local andalusite. This suggests sillimanite follows andalusite.

Inzie Head Gneisses

Sillimanite has been found in this area, but not coexisting with andalusite. It occurs in strongly retrogressed rocks associated with decussate biotite and exsolved opaques. The textures of these rocks are very similar to some retrogressed rocks in Glen Muick and Cromar.

4.7 Andalusite-Sillimanite Relationships: a discussion

Andalusite has been found to postdate peak metamorphic sillimanite in all rocks examined from along Deeside. Peak metamorphic conditions have been substantially obscured in this region. These conditions reached sillimanite-K feldspar in Glen Muick and Cromar. To the east the nature of the peak metamorphic conditions remains to be established. Porteous (1973) briefly describes other occurrences of andalusite from Deeside (including some of the examples discussed above) which are

apparently texturally similar. There is no early andalusite established from along Deeside (c.f. Porteous, 1973; Chinner and Heseltine, 1979). The origin of this andalusite, contact or regional retrogressive remains to be established.

Elsewhere there is apparently evidence for sillimanite later than andalusite. This situation occurs in the aureoles of the Newer Gabbros and along the Stonehaven coast (Booth, 1984). In other areas the evidence is limited to muscovitised andalusite accompanied by fibrolite. This is not totally conclusive as the muscovitisation might postdate fibrolite growth (Kwak, 1971). The texture is tentatively interpreted as indicating the progress of the reaction andalusite \rightarrow fibrolite.

4.8 Deeside Andalusite: Contact or Regional

The Deeside and Glen Muick areas contain considerable outcrops of Newer Granite. If the margins have shallow dips much of the retrogression observed might be attributable to them. However it does appear that many occurrences of andalusite are not spatially associated with these bodies.

There are a number of arguments for supposing that andalusite associated with staurolite is of regional origin:

(1) staurolite is normally replaced by cordierite in Newer Granite Aureoles, as in the Glen Gironck area.

(2) the grain size of micas in these retrogressed rocks is usually much larger than that in clear contact metamorphic hornfelses, although they are of lower grade.

(3) The M/FM of biotite in andalusite-staurolite-biotite assemblages is appropriate to a regional metamorphic event (cf M/FMs in this assemblage in Hudson, 1980).

(4) the rock types occur over a large area not obviously associated with the Newer Granites.

(5) regional retrogressive staurolite is also known from other parts of the Dalradian in the sillimanite zone (Chinner, 1961; Ashworth, 1975).

(6) in the sillimanite zone of the Connemara Dalradian late andalusite of apparently similar aspect occurs (see Badley, 1976; also Yardley, 1976; Treloar, 1982).

None of these arguments can be regarded as unequivocal.

Against this interpretation might be cited the common association of the andalusite with cordierite, generally assumed (reasonably?) to be entirely of contact metamorphic origin in this part of the Dalradian. Naggar and Atherton (1973) describe similar contact metamorphic assemblages from the Irish Dalradian.

In summary it may be stated that similar textures and assemblages might be expected to arise from regional uplift and retrogression and from contact metamorphic effects. It is difficult to separate the effects of these two different events.

4.9 Kyanite-Andalusite Isograd

Chinner and Heseltine (1979) defined a kyanite andalusite isograd in NE Scotland (figure 4.1). Along its western extent it occurs in a sillimanite free area and along its eastern extent it lies within the sillimanite zone. Over much of its course a distinction is required between regional and contact metamorphic andalusite. This was attempted by Chinner and Heseltine (1979) on the grounds of whether the andalusite did or did not coexist with regional metamorphic biotite. The distinction between regional and contact metamorphic biotite was made in large part on the grounds of the M/FM of this phase.

The course of the isograd in the Glen Muick and Cromar areas will first be considered. Chinner and Heseltine (op. cit.) describe a number of supposed regional andalusite occurrences in Glen Muick and Cromar. These are detailed in figure 4.19. The andalusite at Camlet in Glen Gironck lies

very close to the margin of a Newer Granite. The hill above consists of hornfelsed metapelites intermixed with smaller apophyses of Newer Granite. A few hundred metres to the west one is entirely within the Granite. In the less hornfelsic rocks andalusite overgrows a regional muscovite biotite schistosity. Garnets are replaced by masses of shimmer aggregate and foxy red contact metamorphic biotite. Where staurolites occur they are surrounded by reaction rims of cordierite. This andalusite is concluded to be of contact metamorphic origin. Regional kyanite occurs from several localities to the north. Other occurrences of andalusite in the Glen Muick area (not described by Chinner and Heseltine, 1979) have been found to be late. Some are certainly of contact origin. Others may be regional. However their lateness means that they cannot have been in equilibrium with early kyanite.

Chinner and Heseltine (1979) identified andalusite as regional in origin if it coexisted and was associated with regional biotite. In some rocks from Glen Girnock it has been found that contact metamorphic andalusite is associated with regional biotite. Andalusite often seems to appear before extensive recrystallisation of regional biotite is induced. This casts doubt on the criteria used by Chinner and Heseltine to separate the different generations of andalusite. It is possible that other "regional" andalusite occurrences to the west which are close to the margins of Newer Granites are in fact thermal in origin. However south of Braemar the square shaped aggregates of kyanite are accepted as indicative of the former presence of regional andalusite. This conclusion is supported by the relatively low pressures calculated for this area (chapter 6).

The sequence of development of aluminosilicate polymorphs in Glen Muick is :

kyanite → sillimanite → andalusite

The early kyanite is inferred on the basis of the sillimanite aggregate pseudomorphs. The implication is that kyanite was never in equilibrium with andalusite in the Glen Muick area and that therefore the andalusite-kyanite isograd did not exist in this area. Two alternatives might be envisaged at this stage:

- (1) the andalusite-kyanite isograd occurs further to the north.
- (2) kyanite and andalusite were never in equilibrium within most of the present sillimanite zone and therefore a kyanite andalusite isograd only existed outside the sillimanite zone. The distinction between these two hypotheses rests on the distinction between regional and contact metamorphic andalusite in the Glen Muick and Cromar areas. If the andalusite is regional the implied pressure decrease would suggest that no andalusite kyanite isograd existed before the development of a sillimanite zone. The high pressures estimated for rocks in this area (see chapters 3 and 6) is furthermore inconsistent with aluminosilicate triple point pressures and a simple isobaric overprint model for P-T evolution in this area. If a kyanite andalusite isograd did exist within the sillimanite zone, at any time, then increasing temperatures would cause the position of the isograd to move geographically with time. A different isograd would be valid at each different time. Rocks should show the sequence of polymorph development kyanite → andalusite → sillimanite. It could be suggested that the isograd represents the locus of points, at which kyanite and andalusite were in equilibrium, immediately before replacement by sillimanite (i.e. rocks at triple point conditions). In this particular case the isograd would be strongly diachronous and not have the pressure temperature significance, assumed in isogradic syntheses.

A number of andalusite occurrences have been described above from various localities along Deeside. These show late andalusite and are

apparently texturally similar to those described briefly by Porteous (1973). There is apparently no early andalusite along Deeside.

If a kyanite zone existed adjacent to an andalusite zone within the present sillimanite zone it should be possible to delimit areas where sillimanite formed after kyanite and areas where it formed after andalusite. The northernmost occurrence of probable pseudomorphs after kyanite is near Glen Tanar (figure 4.19) while the southernmost occurrence of probable early andalusite is on Donside. There is thus a wide area in which there is no evidence of early andalusite or kyanite. This may be a "primary" sillimanite zone. This is compatible with the second suggestion which suggests the absence of any andalusite-kyanite isograd in the sillimanite zone. The problem is that although P-T paths may be defined locally the regional contemporaneity of mineral zones must be defined geochronologically. It seems likely that Buchan andalusite zone conditions were not contemporaneous with Barrovian kyanite zone conditions.

It is notable that there is a large area over which sillimanite may coexist with one of the other aluminosilicate polymorphs while andalusite very rarely coexists with kyanite. This is true both in the Dalradian and a number of other terrains (e.g. Hollister, 1969; Kwak, 1971; Rumble, 1973). In the Dalradian this fact was originally attributed to a polymetamorphic hypothesis i.e. that sillimanite is late as it "overprints" other metamorphic zones over wide areas while andalusite and kyanite are contemporaneous as they are separated by a sharp isograd and do not significantly overprint each other (Johnson, 1963; Chinner, 1966). These observations may alternatively be attributed to :

- (1) the relative kinetics of the different polymorph transformations.
- (2) the complexities of fluid interactions during migmatization and partial melting.

Inversion of andalusite to kyanite or vice versa may be kinetically fairly easy while the transformation of andalusite or kyanite to sillimanite may be kinetically fairly hard (Hollister,1969).

Along the western part of the andalusite kyanite isograd there is little evidence for andalusite or kyanite having existed prior to the other polymorph, in areas near the isograd. Pseudomorphs are found which provide some evidence for the reaction andalusite \rightarrow kyanite (Chinner and Heseltine,1979). This lack of overprinting might be explained by tectonic attenuation of the zone of overprinting. For instance this could have occurred as a result of the extensional deformation (Coward,1983b) in the Portsoy Slide. Alternatively replacement may not have resulted in the formation of pseudomorphs.

The sillimanite overprint might be related to the fact that equilibration in partially melted terrains may occur over a wider P-T range than normal. Below the melting in isograd rocks will rapidly dehydrate on cooling owing to the progress of hydration reactions. In areas containing partial melts fluids may be released on cooling promoting retrograde reaction. Fibrolite might be produced during such retrograde cooling and fluid release. As noted above it often seems that fibrolite is concentrated in retrograde rocks. Retrograde metastable persistence of kyanite is of course more likely than prograde metastable persistence. The movement of the varying fluids likely to be present in this sort of environment might result in fibrolite growth in some rocks. Lower temperature examples of sillimanite coexisting with another polymorph where migmatization has not occurred often show better defined isograds (e.g. Truchas Peaks, Grambling,1981).

"Overprinting" in this manner is not necessarily a suitable criteria by which to separate metamorphic events. The extent of overprinting is not necessarily a measure of the amount by which metamorphic conditions may

have changed, the amount of overstepping of a given reaction or the regional contemporaneity of mineral zones.

4.10 Sillimanite versus Deformation

Vernon and Flood (1977) have suggested criteria by which harmonious fibrolite may be distinguished from disharmonious fibrolite. Such criteria may show whether sillimanite grew before final grain boundary adjustment. Fibrolite occurrences from the Dalradian will be considered in the light of these criteria.

Muscovites commonly contain single fibrolite needles or swirls of fibrolite. These occur as randomly orientated often complexly folded aggregates or as a trail of inclusions (see Harte and Johnson, 1969). Inclusion trails are often remarkably parallel to each other throughout a thin section (see figure 4.10). Trails in muscovite may be continuous with trails in adjacent minerals such as quartz. In such circumstances it is concluded following Vernon and Flood that the fibrolite trails grew before the final adjustment of grain boundaries. Interpretation of the swirls of fibrolite in muscovite by the reaction model of Carmichael (1969) would suggest that the fibrolite grew later than the muscovite. The above observation suggests that this is sometimes not the case.

Such continuous parallel fibrolite trails in randomly orientated porphyroblastic muscovite occur from a number of areas. They occur in the retrogressed rocks in Cromar and at Maryculter, in upper Glen Mark, in west Glen Muick and sometimes in Glen Clova and the Duchray Hill Gneiss. In Glen Clova staurolites and tourmalines (135B) also include fibrolite trails. Late staurolite has formerly been reported from this area along with late kyanite (Chinner, 1961). In the Duchray Hill Gneiss, Glen Clova and in other margins near the margins of the sillimanite zone fibrolite is more often concentrated along grain boundaries and as radiating aggregates from these boundaries.

In the southern part of the sillimanite zone sillimanite is late and commonly displays features indicating that it grew after the final adjustment of grain boundaries between minerals (see Harte and Johnson, 1969). It is often concentrated along grain boundaries. In the northern part of the area in Glen Muick fibrolitic sillimanite was probably present before the final deformation as it commonly shows evidence of being more compatible with other minerals.

In the north prismatic sillimanite lies within the foliation and is often deformed around garnet. In areas of strong late D_2^m folding aggregates of prismatic sillimanite are often aligned axial planar to the folds. These aggregates are then deformed by later monoclinial folds. In upper Glen Mark, Glen Muick and Cromar fibrolite trails are aligned parallel with the foliation. Muscovites replacing probable earlier kyanite are deformed indicating that kyanite disappeared before the final deformation.

Sillimanite predated the last major deformation in the north, but postdated it in the south (see also Harte and Johnson, 1969). Since neither sillimanite growth or the last deformation event may be reasonably treated as a time reference frame no inferences may be drawn regarding the relative timing of sillimanite growth. Note the reverse sense of diachroneity for staurolite and garnet versus deformation in Glen Esk, reported by Dempster (1984).

4.11 Distribution of Aluminosilicate Zones

In figure 4.20 a zonal map of the aluminosilicate zones is presented, based on the work of previous authors modified by the present discussions. In particular the following points should be noted:

(1) two possibilities are shown for the andalusite-kyanite isograd: a northward displacement or its absence within the sillimanite zone.

(2) Glen Girnock to the west of Glen Muick lies entirely within the kyanite zone.

(3) the whole of the area to the west of the andalusite-kyanite isograd lies within the kyanite zone. A possible exception is the Ailnack area where garnet chlorite may be stable (see chapter 2).

4.12 DISCUSSION

The evidence presented in this chapter has P-T implications for the evolution of the NE Dalradian area. The hypotheses of Chinner (1966) and of Harte and Hudson (1979), that an isobaric overprint occurred, require that kyanite formerly existed in equilibrium with andalusite within the sillimanite zone and that later temperature rise brought temperatures into the stability field of sillimanite. The fact that andalusite along Deeside is late necessitates appeal to other hypotheses. One possibility is that the andalusite-kyanite isograd is in error and must be displaced to the north. The next possibility is that the P-T path suggested by Chinner is wrong. The sequence kyanite → sillimanite → andalusite in Glen Muick may in part be a regional sequence relating to uplift. The relatively high pressures calculated for Glen Muick support this hypothesis of uplift. Different P-T paths are likely to refer to different crustal segments if deformation is continuing during metamorphic evolution (see figure 4.21). To the south of Glen Muick the net reaction kyanite → sillimanite may reflect decompression accompanied by some heating (Wells, 1979). On the Stonehaven coast the reaction andalusite → sillimanite is more appropriate to an isobaric heating model while to the west of the sillimanite zone the reaction andalusite → kyanite suggests pressure increase. Of course it is not envisaged that all the P-T paths represent synchronous metamorphic

evolution. In an actively deforming terrain it is to be expected that different crustal segments will record different P-T paths.

Another problem is the relative timing and evolution of isograds between the aluminosilicate zones. Chinner (1966) suggested that the sillimanite zone was later because of its "overprinting" relationships. No kyanite-andalusite isograd may ever have existed within the sillimanite zone. It is quite possible that a sillimanite zone existed contemporaneously with other zones. Overprinting relationships of this type are not useful in evaluating the temporal relationships of the different zones except locally. The evolution in time and space of the inversion isograds must be elucidated with the aid of local polymorph sequences and the use of geochronological evidence.

4.13 CONCLUSIONS

Prismatic sillimanite growth in Glen Muick was synchronous with the last episodes of deformation. It postdates kyanite, but predates andalusite in Glen Muick and along at least some parts of Deeside. In the north sillimanite appears to postdate andalusite. The sequence kyanite → sillimanite → andalusite in Glen Muick indicates that an andalusite kyanite isograd never existed here. Andalusite in this area may be contact metamorphic and the isograd may lie to the north of Deeside. Alternatively the andalusite may be regional and the isograd never existed within most of the sillimanite zone. The isobaric overprint model may be wrong. Proposed P-T paths are shown in figure 4.22. In either case there is a large area within which there is no evidence for either a primary andalusite or kyanite zone. It is suggested that a primary sillimanite zone is quite likely.

The large area over which andalusite or kyanite coexist with sillimanite is explained as a consequence of the abundant retrograde fluids present or the relative kinetics of the transformations rather than

to any polymetamorphic event. The apparent overprinting does not mean that sillimanite growth is a separable event.

Fibrolite and sillimanite are earlier relative to deformational events in the Glen Muick area than in the extreme south of the sillimanite zone.

CHAPTER 5

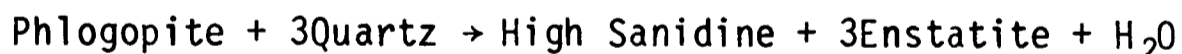
THERMODYNAMICS OF KCMASHCO₂ EQUILIBRIA

In this chapter experimental data in the system KCMASH₂CO₂ will be analysed in order to derive a dataset for a number of phases. This will facilitate the calculation of a number of reactions useful for geothermobarometry and volatile fugacity calculations.

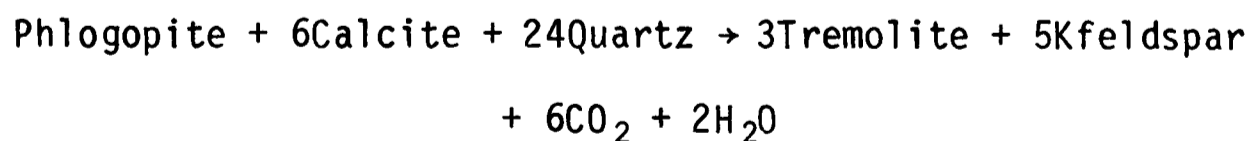
The synthesis and review of thermodynamic data by Helgeson et al. (1978) covers all the phases of interest here except pyrope. More recently Wood and Hollaway (1984) have studied high pressure phase equilibria in the anhydrous system, CMAS. This study relies more on calorimetric determinations of enthalpies of solution from the work of Charlu et al. (1975; 1978). The Helgeson dataset might be improved in view of subsequent data and information. It might be criticised on the following counts in the light of this more recent data.

(1) Data for the system KMASH rely largely on reactions involving cordierite. With much debate about the role of water in the stabilisation of cordierite (Newton and Wood, 1979; Lonker, 1982; Martignole and Sisi, 1982) it may be unwise to attempt calculation of the thermodynamic properties of other phases using reactions involving cordierite.

(2) Reactions involving phlogopite are not self consistent. In particular the reaction:



(Wones and Dodge, 1966) is not consistent with other phlogopite equilibria such as:



for which contradictory experimental results exist (Hewitt, 1975; Hoschek, 1973). Some further data on phlogopite are now available and may help to further constrain further the thermodynamic properties of phlogopite.

(3) The thermodynamic data of Helgeson et al. (1978) for chlorite do not reproduce some experimental data and appear to be inconsistent with data from natural assemblages (Hoschek, 1980; Graham et al., 1983).

(3) The Helgeson et al. dataset does not utilise recent high pressure experimental data and does not include data for pyrope.

(4) Thermodynamic data were extracted using ideal mixing of gases.

Recently Kerrick and Jacobs (1981a) have presented a modified *hard* sphere Redlich Kwong equation to describe the non ideal mixing of CO₂-H₂O mixtures. This equation provides good fit to the slopes of experimentally determined mixed volatile equilibria (Jacobs and Kerrick, 1981b).

(5) Some new experimental data are available.

In this chapter it will be attempted to derive a dataset for a number of phases in the system CKFMASHCO₂. In so doing it will be attempted to reproduce acceptable agreement with :

(1) high pressure anhydrous phase equilibrium as studied by Wood and Hollaway (1984) in CMAS.

(2) low pressure, including mixed volatile equilibria.

(3) available calorimetric data, particularly that of Charlu et al. (1975; 1978).

5.1 CALCULATION METHODS

A subset of the phases considered by Helgeson has been considered with the specific intention of deriving useful, but geologically unconstrained equilibria of use for geobarometry or volatile fugacity calculations. This subset of phases is listed in table 5.2. Calculations of mixed volatile reactions have been carried out using a computer program, incorporating the computer program of Jacobs and Kerrick (1981) which calculates the fugacities of water and carbon dioxide using the MHSRK equation of state of Jacobs and Kerrick (1981a). This program is listed in appendix B. A brief summary of thermodynamic methods is given in

appendix C. For the calculation of most reactions expansivities and compressibilities have been neglected, a reasonable procedure at relatively low pressures and temperatures. At higher pressures the effect of these parameters has been considered. Where compressibilities and expansivities are considered, volumes at the pressure and temperature of interest are calculated according to equation 17 in appendix A. Reactions have been calculated according to equation 23. Some reactions require extrapolation of heat capacities beyond 1000K, for which experimental heat capacity measurements are often not available. Where necessary this extrapolation has been performed using the approximation: $\Delta C_{p,T}^r = \Delta C_{p,1000K}^r$, following Wood and Holloway (1984).

A linearly independent set of experimentally well constrained reactions has been considered in KCMASHCO₂. Entropies have been taken from the literature, except for a number of phases mentioned below. Using these entropies acceptable limits to the enthalpy of reaction have been derived from the experimental data. These enthalpies have been adjusted to reproduce experimental data referring to reactions which are linear combinations of this initial set, ^{by trial and error.} These reactions are listed in tables 5.6, 5.7 and 5.8.

A number of reactions in complex systems are considered in order to derive experimentally unconstrained reactions. This may result in smaller errors than working in many simpler systems, combining these systems at a later stage, if it is desired to constrain reactions in complex systems.

5.2 DATA SOURCES

Sources of data are given in tables 5.2 through 5.5. Entropy data have been taken in most cases from Robie et al. (1978). For the phases talc and zoisite heat capacity data from Robie et al. (1978) and Perkins et al.

(1980) respectively are only valid for a limited range of temperatures. Therefore heat capacity data from Holland (1981) have been used for these phases, which utilise estimated heat capacities at high temperature. Pyrope and grossular entropies and heat capacity data are from Haselton and Newton (1980). Aluminosilicate entropies are from Robie and Hemingway (1984). Sillimanite has been assumed to be completely ordered following Robie and Hemingway (1984). The entropy at 298.15K for muscovite is taken as 287.86JK^{-1} ; less than the value in Robie et al. (1978) as a disordered muscovite will not reproduce the Clapeyron Slopes of the reactions studied by Chatterjee and Johannes (1974), (Helgeson et al., 1978). 2.6JK^{-1} has been added to the entropy of anorthite to account for possible disorder (Perkins et al., 1980; Wood and Holloway, 1984). The entropies of 14A MgClinocllore and of phlogopite have been calculated by summation following Helgeson et al. (1978), (see table 5.4).

Volumes have been taken from Robie et al. (1978) except for zoisite and 14A MgClinocllore which come from the compilation on Helgeson et al. (1978). Expansivities and compressibilities come from the compilation in Wood and Holloway (1984) after Clark (1966), Brace et al. (1966) and Hazen and Finger (1978).

5.3 REACTIONS INVOLVING DOLOMITE AND CALCITE:

Dolomite becomes disordered towards higher temperatures (see Helgeson et al., 1978). This degree of disordering will be very small at the temperatures of most of the experiments considered. In this study the dolomite heat capacity given by Krupka et al. (1979) and listed in Robie et al. (1978) have been used. This is for dolomite in an unreported state of order. Helgeson et al. (1978) estimated a heat capacity for dolomite which incorporated this disorder. Use of the Krupka et al. (1979) or the estimated Helgeson et al. entropy for dolomite will result in very small

differences in calculated P, T and X_{CO_2} (Helgeson et al., 1978).

A number of reactions involve both dolomite and calcite. Coexisting calcite and dolomite show solid solution. Allowance must therefore be made for this solid solution. Previous studies (e.g. Skippen, 1974) have used magnesite and calcite as components in their reactions and calculated activities of these two components using the expressions of Gordon and Greenwood (1970). In order to make reactions, involving coexisting calcite and dolomite, consistent with those involving only calcite or only dolomite thermodynamic data for the reaction :



are necessary. Taking data from Robie et al. (1978) the error in this correction will be greater than the magnitude of the effect to be corrected for. Calcite activities have therefore been calculated from the expression in Gordon and Greenwood (1970), derived by analysis of the calcite dolomite solvus using the components calcite and magnesite. Dolomite activities have been calculated from the dolomite compositional data of Anovitz and Essene (1982) using $CaMg(CO_3)_2$ and $Ca_2(CO_3)_2$ as components. A subregular solution model has been used (see Saxena, 1973; appendix C) and the mixing parameters have been evaluated at different temperatures. Results are given in table 5.1. The effect of pressure has been ignored as this is minimal (Goldsmith and Newton, 1969). Application of the derived activities to the experimental data show that solid solution between calcite and dolomite have very little effect on calculated reactions even at temperatures up to 800°C. Calculated ΔH would be affected by $\sim 500J$. The effect of this solid solution has been incorporated into the calculation of the reactions shown in the figures.

5.4 DISCUSSION OF PHASE EQUILIBRIUM DATA

ALUMINOSILICATE POLYMORPHS

The enthalpies of reaction for reactions between polymorphs are in agreement with those adopted by Robie and Hemingway (1984).

CASHCO₂

In this system a number of inconsistencies arise between the dataset and experimentally determined equilibria. These will be discussed by reaction.

Calcite + Quartz → Wollastonite + CO₂ (figure 5.13)

Experimental data by a number of workers exist in this system: Harker and Tuttle (1956), Greenwood (1967), Ziegenbein and Johannes (1974) and Jacobs and Kerrick (1981). The studies of Harker and Tuttle (1956) and Greenwood (1967) may have overestimated temperature according to Jacobs and Kerrick (1981b). The Greenwood data at 1kb are inconsistent with the data of Ziegenbein and Johannes (1974) and of Jacobs and Kerrick (1981). The adopted ΔH_{298} of 91.5kJ reproduces most of the data. It is not consistent with the data of Harker and Tuttle (1956) or of Greenwood (1967) at 1kb. It does reproduce the experimental data of Greenwood at 2kb, of Ziegenbein and Johannes (1974) and of Jacobs and Kerrick (1981). The calculated phase equilibrium boundary may be slightly too high by comparison with some of the data of Ziegenbein and Johannes (1974).

Anorthite + 2Wollastonite → Grossular + Quartz (figure 5.10)

Experimental determinations exist by Newton (1965), Boettcher (1970) and Huckenholz et al. (1975), at relatively low pressure, and by Hays (1967) and Windom and Boettcher (1976), at relatively high pressure. The low temperature experiments of Huckenholz et al. (1975) and of Newton (1965) are inconsistent. The entropy data used here will not reproduce a Clapeyron Slope consistent with both high and low pressure experiments. Expansivities and compressibilities have little effect on calculated

pressures. A ΔH_{298} of -46.5kJ reproduces most of the experimental data except the high pressure experiments of Hays and Windom and Boettcher by some 2kb. Only an unreasonably large increase in anorthite entropy could produce agreement between both high and low pressure experiments. Such entropy adjustments would also cause disagreements between experimentally determined and calculated positions of other equilibria.

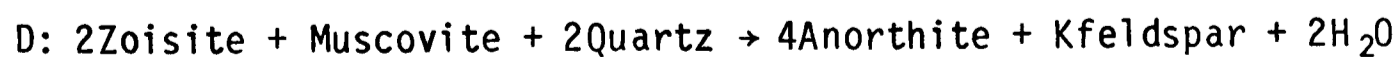
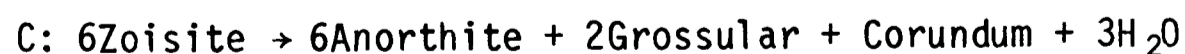
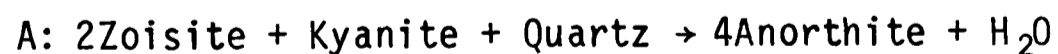
3Anorthite \rightarrow Grossular + 2Kyanite + Quartz (figure 5.10)

The experimental determinations by Goldsmith (1981), Hays (1967), Hariya and Kennedy (1968) and Schmid et al. (1978) imply various positions for this equilibria. The calculated curve agrees with all the reversals of Goldsmith (1981), the preferred experimental determination. The Goldsmith data implies somewhat lower pressures than the other determinations.

Calcite + Alsilicate + Quartz \rightarrow Anorthite + CO_2 (figure 5.6)

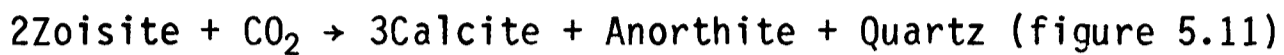
Entropy data for the phases involved, combined with Jacobs and Kerricks (1981) MHSRK equation of state fails to reproduce the slopes of either this reaction, with andalusite or with kyanite. An ideal mixing approximation would produce a better fit (see Jacobs and Kerrick, 1981). The calculated curves in figure 5.6 lie below the experimental data at high X_{CO_2} . If ΔH_{298} was adjusted to reproduce the data at high X_{CO_2} then disagreement would be produced with other experimentally determined equilibria.

Zoisite Reactions (figure 5.9)



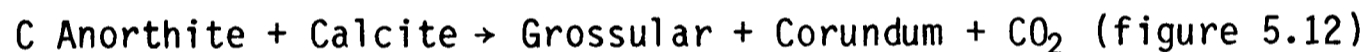
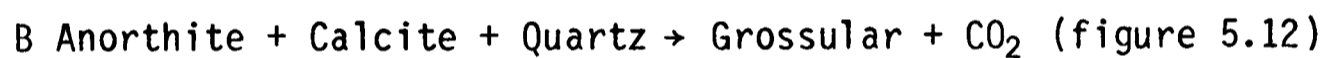
Reasonable fit is provided to the first two reactions. The calculated reaction is consistent with some, but not all of the experimental brackets

of reaction C. For reaction D the calculated reaction curve lies about 15°C higher than permitted by the experimental brackets of Johannes (1980). Use of a different ΔH for reaction D would produce disagreement with other equilibria.



This reaction has been determined by a number of authors with widely differing experimental results (see references in Allen and Fawcett, 1982). The most recent experimental determination of Allen and Fawcett (1982) has used SEM to characterise the phases produced during the reaction. The data used here is entirely consistent with the well defined experimental bracket of Allen and Fawcett (1982).

Decarbonation Reactions

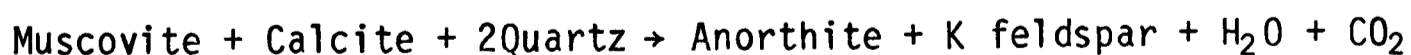


Good fit is provided to these reactions except for reaction A. Limited experimental data for reaction A exists at 1, 2 and 4 kb. The data of Gordon and Greenwood (1970) at 2 kb is inconsistent with that of Hoschek at 1 and 4 kb. The dataset employed here is consistent with only two of the experimental points of Gordon and Greenwood (1970) at 2 kb.

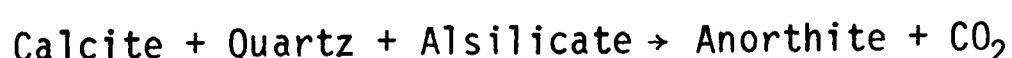
KCASHCO₂

Muscovite Dehydration (figure 5.8)

The experiments of Chatterjee and Johannes (1974) on muscovite dehydration are well fitted by the calculated data.



The experiments of Hewitt (1973) are consistent with a ΔH of 188 kJ (see figure 5.8) which is also consistent with expressions for the reactions:



and $\text{Muscovite} + \text{Quartz} \rightarrow \text{Kfeldspar} + \text{Alsilicate} + \text{H}_2\text{O}$

CMASHCO₂

The fit to the experimental data in this system is shown in figures 5.1 through 5.6 for the low P-T devolatilisation equilibria. Agreement for most equilibria is very good. Errors in calculated reactions might potentially result from consideration of reactions with

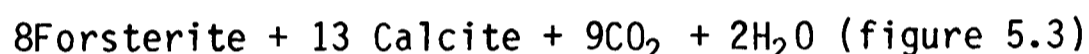
(1) growth of metastable disordered dolomite.

(2) tremolite in various states of disorder.

(see Helgeson et al., 1978).

Relatively poor agreement is obtained for the following reactions:

(1) Tremolite + 11Dolomite \rightarrow



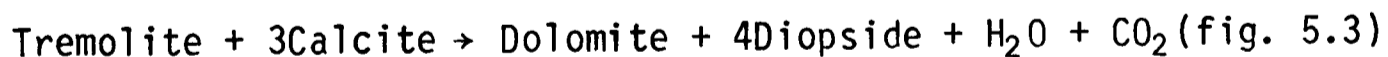
at 1kb, but not at higher pressure.

(2) 3Dolomite + 4Quartz + H₂O \rightarrow Talc + 3Calcite + 3CO₂ (figs. 5.2, 5.4)

for which poor agreement occurs with the 1 and 2kb data of Metz (1970, 1971), but not with the 3 and 5kb data of Metz and the data of Eggert and Kerrick (1981) at 6kb.

(3) poor agreement with the 1kb data of Slaughter et al. (1975) for the reaction : Dolomite + 2Quartz \rightarrow Diopside + 2CO₂ (figure 5.2)

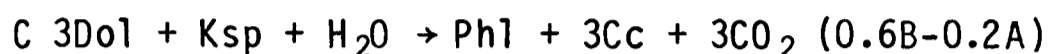
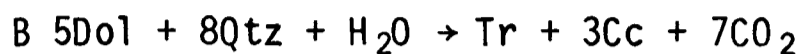
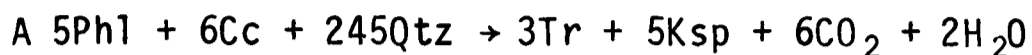
(4) marginal disagreement with the data of Slaughter et al. (1975) for the reaction



Helgeson et al. (1978) in their consideration of this system used much of the experimental data of Skippen (1971). These are for various buffers involving a number of gas phases. As the calculation of the fugacities of CO₂ and H₂O in some of these mixtures may not be easily performed by MHSRK methods these reactions have not been considered.

KCMASHCO₂

Reactions involving phlogopite will now be considered. Experimental data for the following reactions are available.



If experimental data from Hewitt (1975) rather than from Hoschek (1973) is used for reaction A the five reactions are internally consistent. Helgeson et al. (1978) suggested that the experiments of Hoschek (1973) were inconsistent with other data. Agreement between calculated and experimental equilibria for reactions A through D is shown in figures 5.8, 5.5, 5.7 and 5.2. Experimental data for reaction E is given in Hoschek (1980) after Becker (1972). Calculation of this reaction at the experimental conditions of 2 kb abd $X_{\text{CO}_2} = 0.8$ gives a temperature of 469°C in good agreement with the experimental temperature of 465°C.

5.5 HIGH PRESSURE PHASE EQUILIBRIUM DATA

High pressure phase equilibrium data in CMAS have been calculated by Wood and Holloway (1984). The entropy data of Wood and Holloway (1984) are identical to that used here for all phases except for sillimanite and kyanite. Reactions will be discussed briefly individually. Calculations of these high pressure phase equilibria have been performed using the methods of Wood and Holloway (1984) e.g. for the calculation of the activity of enstatite in aluminous enstatite.

Enstatite + Corundum → Pyrope

An experimental bracket for this equilibrium has been measured by Newton and is quoted in Wood and Holloway (1984). The experiments give

$P=16.25+0.25\text{kb}$ at 850°C while calculations from the dataset give 16.0kb at 850°C .

4Enstatite + Spinel \rightarrow Pyrope + Forsterite (figure 5.14)

Experimental determinations by Danckwerth and Newton (1978) and Perkins et al. (1981) are shown in figure 5.14. The calculation of this reaction performed by Wood and Holloway (1984) is compatible with the data presented here. Spinel disordering has been modelled following Wood and Holloway (1984).

3Enstatite + Sillimanite \rightarrow Pyrope + Quartz

Experiments of this reaction in MAS have been performed by Hensen and Essene (1971) and Perkins (1983). Calculations give the curve in figure 5.14 in reasonable agreement with most of the experiments.

Anorthite + 4Enstatite \rightarrow Pyrope + Diopside + Quartz

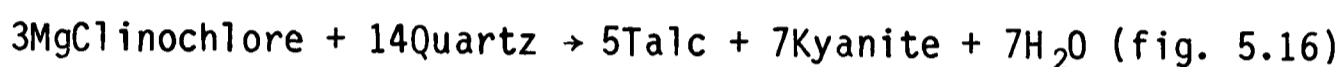
Determinations by Hansen (1981) and Perkins (1983) are reproduced reasonably, particularly if non stoichiometry in the clinopyroxene is taken into account (see Wood and Holloway, 1984). The data used here give a reaction about 450bars lower than that calculated by Wood and Holloway (1984), the approximate position of which is shown in figure 5.15. Non stoichiometry in the clinopyroxene will lower the position of this reaction.

Other Reactions

The dataset here is similar to that adopted by Wood and Holloway (1984). Although no calculations have been performed on other experimental data in this system the data here should show agreement within a few hundred bars to the calculations of Wood and Holloway (1984) and this dataset should therefore agree with the other equilibria considered by Wood and Holloway (1984).

5.6 CHLORITE

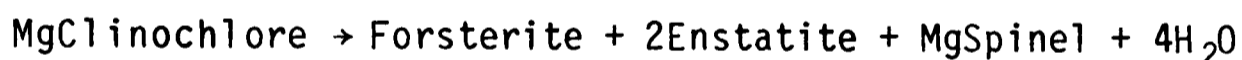
Extraction of thermodynamic data for 14\AA MgClinochlore from the experimental data is complicated by the variable tschermak substitution to be expected in chlorite and other phases such as biotite and tremolite in the aluminous experimental systems considered. Any thermodynamic data and calculations will obviously be subject to greater uncertainty than for other phases considered here. Four reactions involving MgClinochlore are considered, none involving cordierite (table 5.8).



This reaction has been determined by Massone et al. (1983) at pressures of 11 and 16kb. No details are given in the paper of chlorite and talc compositions, but it will be attempted to use the data nevertheless.

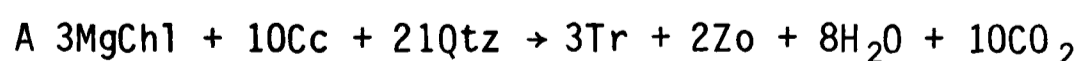


This reaction determined by Bird and Fawcett (1973) has been used to extract data for MgClinochlore by Helgeson et al. (1978).

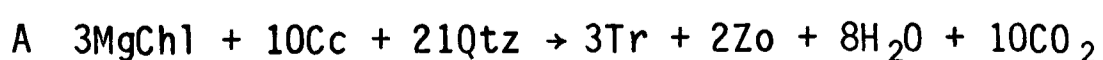


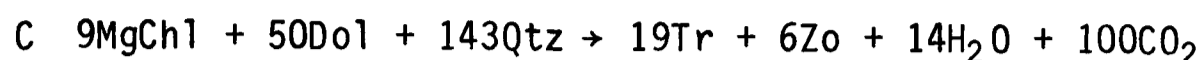
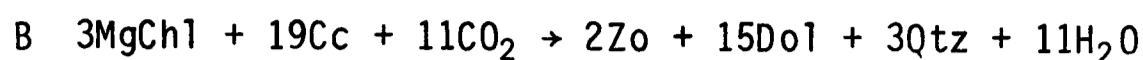
This reaction determined by Fawcett and Yoder (1966) requires the calculation of spinel disordering. The reaction has been calculated using the spinel disordering model of Wood and Holloway (1984).

Best (1978) has considered a number of reactions in CKMASHCO₂ involving MgChlorite. Neither of his experimental starting compositions correspond to the composition of MgClinochlore. Bests experimental data for penninite for the reaction:

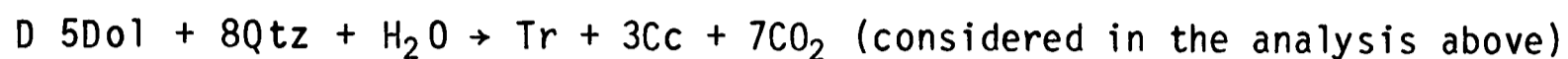


has been used. In this analysis the activity of MgClinochlore has been calculated using the activity model in chapter 6. The reactions studied by Best (1978) are listed below:





They lie around an invariant point also including the reaction:



The reactions studied by Best (1978) are internally consistent, but the two dolomite bearing reactions are not consistent with reaction D as calculated in the dataset of this study. This may be the result of metastable disordered dolomite in Best's experiments (Hoschek, 1980). The agreement between calculated and experimentally determined equilibria is shown in figures 5.16 and 5.17. As can be seen agreement is not obtained with all the experiments. The data adopted for MgClinocllore represent a compromise between the different experiments.

5.7 THERMODYNAMIC DATA FOR THE PHASES

The heats of formation from the oxides at 298K as estimated from the reactions considered here are shown in table 5.9. These are compared with direct calorimetric measurements of heats of formation. The heat capacity data of table 5.6 and additional data from Robie et al. (1978) have been used to return heats of formation at other temperatures to 298K. When so doing it has been assumed that use of these heat capacities introduces no additional error to that quoted in the literature sources. The enthalpies of formation have been adjusted to provide best fit to the calorimetric data.

The phases wollastonite, grossular, pyrope, forsterite and diopside are within the errors of the determinations of Charlu et al. (1975, 1978). The heat of formation of forsterite preferred by Robie et al. (1984) is about 5kJ less negative than that preferred here. The heat of formation of anorthite lies between the measurements of Charlu et al. (1978) and Newton et al. (1980). The anorthite data is however inconsistent with that quoted in Robie et al. (1978). The heat of formation of enstatite is not

consistent with the data of Charlu et al. (1975) or of Shearer and Kleppa (1973), as noted by Wood and Holloway (1984). However the data of Torgeson and Sahama (1948) for clinoenstatite differs little for that given here for enstatite.

Tremolite has a heat of formation within the errors of the data of Weeks (1956) while dolomite is slightly outside the permitted limits of Robie et al. (1978). The heat of formation of talc is totally inconsistent with that reported by Barany (1963); such an observation being in agreement with Helgeson et al. (1978). The heat of formation of calcite is in good agreement with that reported in Robie et al. (1978). The values for the aluminosilicates are in good agreement with the data of Anderson and Kleppa (1969), Anderson et al. (1977) and Charlu et al. (1975).

5.8 CALCULATION OF SOME REACTIONS IN KCMASHCO₂

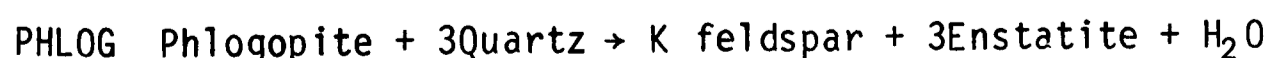
The reactions listed in table 5.10 have been calculated from the dataset.

OPX & CPX: The two reactions were calibrated by Newton and Perkins (1982) for use as barometers. These barometers are here calibrated from experimental data as well as from calorimetric data. The derived barometers give pressures in agreement with each other when tested on the data of Newton and Perkins (1982) and read about 1kb lower than the barometers of these authors. The Newton and Perkins calibration requires an empirical correction in order to make the two barometers agree.

ALSIL: This barometer gives pressures within a few hundred bars of that of Newton and Haselton (1981).

REACTIONS INVOLVING PHLOGOPITE

The following reactions involving phlogopite may be calculated:



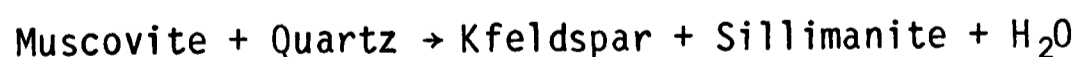
PHL Phlogopite + 2Kyanite + Quartz → Pyrope + Muscovite

PHLOG* Phlogopite + Sillimanite + 2Quartz → Pyrope + K feldspar + H₂O

In the kyanite field the reaction PHL has very high dP/dT . Its position has been calculated using the thermodynamic data in table 5.10. It may be applied to many of the rocks studied here from the Dalradian, as is done in table 5.11. It can be seen that temperatures, using the thermodynamic data of this chapter, together with the activity models of the next chapter, are far too low to be credible.

Alternatively the reaction PHL may be calculated from thermodynamic data based on disordered (see Helgeson et al., 1978) phlogopite that appears to have been used in the experiments of Wones and Dodge (1966) on the reaction PHLOG. This experimental determination is inconsistent with other available phlogopite data if the dataset of this chapter is used. Calculations have been performed, based on the Wones and Dodge (1966) experiments with a $\Delta H_{r, 298}$ of 108 kJ. Phlogopite entropy has been increased by 18.67 JK^{-1} to account for postulated complete tetrahedral disorder. The reaction PHL, calculated using this disordered phlogopite data gives higher temperatures when applied to natural rocks (see table 5.11). These are still somewhat on the low side, but are within error of preferred temperature estimates.

The errors involved in the calculation of PHL are relatively small. The calculation could be viewed as the addition of the reactions:



and $\text{Phlogopite} + 3\text{Quartz} \rightarrow \text{Kfeldspar} + 3\text{Enstatite} + \text{H}_2\text{O}$

Thermodynamic data for the first two are relatively well constrained, the former on account of the good experimental determination, the latter on account of the small volume change. Most error will arise from

uncertainties in the third phlogopite dehydration reaction. Natural mineral compositions imply an error in ΔH for PHL of $\sim 10\text{kJ}$ for the ordered model and $\sim 2\text{kJ}$ for the disordered model. It seems that errors in calculations from the dataset should be 5kJ or less implying that only the disordered phlogopite model is acceptable.

Application of PHLOG and PHLOG* to high temperature metapelites (e.g. Mukherjee, 1979, chapter 6) suggests that the ordered phlogopite thermodynamic model predicts $X_{\text{H}_2\text{O}}$ which is too high and often more than one.

The reaction MGMICA calculated from the ordered phlogopite dataset suggests pressures 1.5-2kb lower than other barometers and MGMICA calculated using disordered phlogopite data.

There is thus a suggestion that calculations using data for disordered phlogopite are more appropriate to natural assemblages. It is implied that biotites in many natural rocks are disordered on tetrahedral sites. There is limited independent evidence to support this conclusion. The crystal chemical study of Bohlen et al. (1980) finds that a natural biotite slowly cooled from $\sim 700^\circ\text{C}$ is disordered on tetrahedral sites.

5.9 SUMMARY

The dataset of table 5.9 has been derived from phase equilibrium and calorimetric data in the system CKMASHCO₂. This dataset should reproduce a large number of equilibria of geological interest. A consistent set of barometers has been derived for the system CMAS:

the reactions OPX, CPX and ALSIL. The reaction MGMICA is in good agreement with these barometers if natural biotites are assumed to be Al-Si disordered and thermodynamic data for phlogopite is based on the experiments of Wones and Dodge (1966).

CHAPTER 6

THERMODYNAMIC ESTIMATION OF THE
CONDITIONS OF METAMORPHISM

The methods of equilibrium thermodynamics have been applied to mineral assemblages from different lithologies in the aluminosilicate zones of the E Dalradian in order to ascertain the pressures, temperatures and fluid compositions during metamorphism. In this chapter the methods and calibrations used and the validity of the estimates are discussed. Interpretations in terms of different tectonothermal models are discussed elsewhere. Thermodynamic approximations and methods are detailed in appendix A. Locations mentioned in the text are shown in figure 6.1

6.1 ACTIVITY MODELS

Prior to a discussion of the different thermobarometrical calibrations, activity models for the various phases will be discussed.

Garnet

Non ideality of garnet solid solutions is likely to be significant to a number of geothermobarometrical calibrations. Ganguly and Kennedy (1974) used a a four component symmetric solution model to model this nonideality giving the following expression for the activity coefficient of $\text{FeAl}_{2/3}\text{SiO}_4$, γ_{Fe} :

$$\begin{aligned} RT \ln \gamma_{\text{Fe}} = & W_{\text{FeMg}} (X_{\text{Py}})^2 + W_{\text{CaFe}} (X_{\text{Gross}})^2 + W_{\text{FeMn}} (X_{\text{Spess}})^2 \\ & + (W_{\text{FeMg}} + W_{\text{CaFe}} - W_{\text{CaMg}}) X_{\text{Py}} X_{\text{Gross}} \\ & + (W_{\text{FeMg}} + W_{\text{FeMn}} - W_{\text{MgMn}}) X_{\text{Py}} X_{\text{Spess}} + (W_{\text{FeMn}} + W_{\text{CaFe}} - W_{\text{CaMn}}) X_{\text{Gross}} X_{\text{Spess}} \end{aligned}$$

and similar expressions for the other activity coefficients, where W_{ij} are the Margules parameters. A number of different values have been suggested for these parameters either on the basis of experimental work or the analysis of natural garnets of variable composition and their Fe-Mg exchange with other phases at constant temperature. For instance Ganguly and Kennedy (1974) considered staurolite zone garnet-biotite pairs, (but do not take into account the affect of zoning). Dahl (1980) considers garnet-clinopyroxene pairs from a restricted area.

Experimental work in the system Ca-Fe-Mg has been reviewed by Newton and Haselton (1981). It was suggested that only W_{CaMg} is significant, being given by the relation:

$$W_{CaMg} = 3300 - 1.5T(K) \text{ cal mol}^{-1}.$$

The value of W_{FeMg} is more the subject of debate. Newton and Haselton suggested that it was about zero on the basis of the low well constrained difference $W_{FeMg}^{garnet} - W_{FeMg}^{olivine}$ (O'Neill and Wood, 1981) and the low $W_{FeMg}^{olivine}$ (Sack, 1980). This suggestion is at odds with that of Perkins (in Bohlen et al., 1983b), of a significant W_{FeMg} based on an appraisal of all available data and that of other authors based on indications from natural garnet bearing assemblages (Ganguly and Kennedy, 1974; Dahl, 1980). It has been suggested that garnet almandine-pyrope solutions may be ideal towards the Mg end of the system, represented by the experiments of O'Neill and Wood, but non ideal towards the Fe end represented by natural compositions (Perkins, op.cit). Ganguly and Saxena (1979) suggest such an asymmetric model for the almandine-pyrope join.

No experimental data exist for interactions with spessartine component in garnets. Study of natural FeMg exchange reactions implies that only W_{MgMn} is significant and is given by about 3000cal (Ganguly and Kennedy, 1974; Dahl, 1980). Use of this value and the Ca-Fe-Mg garnet model of Newton and Haselton results in very high garnet biotite exchange thermometer temperatures for Dalradian metapelite garnets. It may therefore be assumed that $W_{MgMn} = 0$, a conclusion in agreement with Hodges and Spear (1982). In summary two models will be used: the Hodges and Spear (1982) suggestion ($W_{ij} = 0$ except $W_{CaMg} = 3300 - 1.5T$) and also the Ganguly and Saxena (1984) model.

Plagioclase

The activity model for plagioclase adopted is that of Newton et al. (1980), based on enthalpy of mixing experiments for high structural state plagioclases. These may be combined with entropies of mixing derived, using various assumptions, by Kerrick and Darken (1975) to give activity composition models for plagioclase. The model which gave best agreement with the partitioning experiments of Orville (1972) was selected. This gives the following expression for the activity of anorthite in plagioclase, α_{An} :

$$\alpha_{An} = (X_{An} (1 + X_{An})^2 / 4) \exp(4.184 \times (1 - X_{An})^2 / RT (2050 + 9392 X_{An})) \quad (R=8.314)$$

This model is strictly valid only for plagioclases in the high structural state. An alternative model is that proposed by Saxena and Ribbe (1972) based on the exchange data of Orville (1972) and of Seck (1971). This model predicts much lower activity coefficients for anorthite in plagioclase.

Muscovite

The activity of the components muscovite and celadonite in the phase muscovite have been calculated using ideal mixing on sites models as described by Powell and Evans (1983) giving the following expressions:

$$a_{MU} = 9.48 X_{K,A}^2 X_{Al,M1}^2 X_{V,M2} X_{Al,T} X_{Si,T}^3 X_{OH}^2$$

$$a_{CEL} = 4 X_{K,A} X_{Mg,M1} X_{Al,M1} X_{V,M2} X_{Si,T}^4 X_{OH}^2$$

It is assumed that Al and Mg are disordered on M1.

Paragonite-Muscovite Solid Solutions

Paragonite-muscovite solid solutions are considerably non-ideal. Activities are calculated using the model of Cheney and Guidotti (1979). Activities of paragonite are given by the expression:

$$a_{PARAG} = \gamma_{PARAG} X_{Na,A} X_{Al,M2}^2$$

Activity coefficients for this join have been presented by Eugster et al. (1972), Chatterjee and Froese (1975) and Blencoe (1977). The solvus is assymmetric and is approximated by a subregular solution model (see appendix A). The following expressions are adopted for the interaction parameters following Pigage and Greenwood (1982):

$$W_{\text{Par}} = 12957 + 0.3138P + 0.7104T \text{ (JbarK}^{-1}\text{)}$$

$$W_{\text{Ms}} = 18015.9 + 0.2389P + 1.6543T \text{ (JbarK}^{-1}\text{)}$$

These are based on the work of Chatterjee and Froese (1975) with pressure dependence from the 8kb data of Blencoe (1977) for the $2M_1$ polymorph.

Biotite

An ideal mixing on sites model was used for biotite (Powell, 1978). Fe-Mg interactions are assumed to be ideal (Schulien, 1980, c.f. Bohlen et al., 1980). This results in the following expression :

$$a_{\text{PHLOG}} = 9.48 X_{\text{K,A}} X_{\text{Mg,M1}}^2 X_{\text{Mg,M2}} X_{\text{Al,T}} X_{\text{Si,T}}^3 X_{\text{OH}}^2$$

where $X_{\text{Mg,M1}} = (1 - X_{\text{V,M1}}) / (1 + \text{Fe/Mg})$ and $X_{\text{Mg,M2}} = (1 - X_{\text{Al,M2}}) / (1 + \text{Fe/Mg})$. It is assumed that Fe and Mg are distributed across M1 and M2 in similar proportions, that Al is located on M1 and vacancies on M2.

Staurolite

The activity of Festaurolite is calculated using the expression :

$$a_{\text{FeSt}} = X_{\text{Fe}}^2 \text{ Ganguly (1972).}$$

Clinopyroxene and Orthopyroxene

The activity of diopside in clinopyroxene is calculated using the expression :

$$a_{\text{DI}} = X_{\text{Ca,M2}} X_{\text{Mg,M1}}$$

and that of enstatite in orthopyroxene by:

$$a_{\text{EN}} = X_{\text{Mg,M2}} X_{\text{Mg,M1}}$$

It is assumed that Na and Ca are located on M2 and Al and Ti on M1. Fe and Mg are located on both sites (Wood and Banno, 1973).

The activity of CaTs component in clinopyroxene is calculated using the model of Wood (1979):

$$a_{\text{CaTs}} = \gamma_{\text{CaTs}} X_{\text{CaTs}}^2 \text{ where } X_{\text{CaTs}}^2 (2 - X_{\text{CaTs}}) = X_{\text{CaTs}}, \quad X_{\text{CaTs}} = X_{\text{Ca,M2}} X_{\text{Al,M1}} X_{\text{Al,T}} X_{\text{Si,T}}$$

Chlorite

The activity of chlorite is calculated by the ideal mixing on sites model given by Graham in Powell and Evans (1983):

$$a_{\text{CLIN}} = 64 X_{\text{Mg,M2}}^3 X_{\text{Mg,M1}}^2 X_{\text{Al,M1}} X_{\text{Al,T}} X_{\text{Si,T}}^3 X_{\text{OH,V}}^8$$

6.2 THERMOMETRY

Garnet-biotite

Temperature variation has been examined primarily using the garnet biotite Fe-Mg thermometer of Ferry and Spear (1978) or various modifications thereof. This differs from other calibrations in that it is experimentally based. Alternatives are the calibrations of Goldman and Albee (1977) based on empirical calibration against oxygen isotope temperatures and that of Thompson (1976) derived by a comparison with a pelite petrogenetic grid.

As pointed out by Ganguly and Kennedy (1974) and Hodges and Spear (1982) a correction should be made for nonideality of garnet solid solutions. The Ferry and Spear thermometer has been modified using the activity models suggested by Hodges and Spear (1982) and Ganguly and Saxena (1984). The affects of possible alternative activity models is shown in table 6.5. Assuming significant W_{MgMn} temperatures become much too high for Fe rich garnets. Problems may arise from possible non ideality of phlogopite-annite solid solutions or the occurrence of other components in biotite e.g. Ti, Mn, Fe^{3+} and variable tschermak substitution. Fe^{3+} substitution is unlikely to be a major problem (Percival, 1983). Mn is never present in significant quantities although Ti is rather high in some high grade biotites and exceeds the recommended

limits of Ferry and Spear (1978) in some sillimanite-K feldspar zone rocks.

The Goldman and Albee version gives temperatures about 50°C lower at 600°C (as calculated by unmodified Ferry and Spear) and about 100°C at 800°C. Below 600°C the two are in reasonable agreement. This probably reflects the tendency of isotopic thermometers to reequilibrate at high temperatures. The Thompson calibration gives results somewhere between the two. The correction for Ca and Mn applied to the Ferry and Spear thermometer following Hodges and Spear (1982) increases temperatures by an average of 30°C and a maximum of about 80°C. The correction is generally much less at higher grades where garnets are less rich in grossular. The Ganguly and Saxena (1984) modification of Ferry and Spear tends to give lower results than the Hodges and Spear modification.

Garnet zoning profiles have been constructed for some of the garnets used for thermometry (see the appendix). Garnet rim compositions have been used in the calculation of temperatures except where garnet centres are homogeneous when edge plateau compositions have been used.

At higher grades rims in immediate contact with biotite have been avoided in order to minimise the possibility of significant retrograde Fe-Mg exchange. In the higher grade areas of Glens Esk, Clova, Muick and the Duchray Hill Gneiss some temperatures appear to be anomalously low. This may be attributed to such retrograde Fe-Mg exchange. In some of the highest grade rocks in Glen Muick and Cromar there is more scatter in Fe/Mg ratios in garnets and biotites. Temperatures have been calculated using average biotite compositions away from garnet and average edge plateau compositions. For instance using extreme Fe/Mg ratios from garnets and biotites from a typical Glen Muick rock would give temperatures varying between 750°C and 850°C.

Garnet-Clinopyroxene Thermometry

The garnet-clinopyroxene Fe-Mg exchange thermometer as calibrated by Ellis and Green (1979) has been applied to metabasite assemblages in the high grade part of the sillimanite zone. The calibrations of Ganguly (1979) and Saxena (1979) give higher results by 60 to 100°C. The empirical calibration of Dahl (1980) gives rather scattered results. The Ellis and Green calibration appears to be preferable in that it gives results more reasonable and consistent than others (Johnson et al., 1983). It is based on experimental work at very high pressures where the garnets are similar to normal metabasite garnets, but the pyroxenes contain large amounts of Ca-tschermak component and are hence unlike lower pressure pyroxenes. A correction is applied for variable Ca in garnet, but not for interactions involving CaTs component in the clinopyroxene.

Garnet amphibole thermometry

Graham and Powell (1984) have empirically calibrated a garnet-amphibole Fe-Mg exchange thermometer by reference to the Ellis and Green calibration of the garnet-clinopyroxene thermometer. This assumes that all Fe is divalent and hence must be applied to amphibolites of uniform f_{O_2} . A correction for nonideality in the garnet due to grossular component has been applied.

Ilmenite-clinopyroxene thermometry

The ilmenite-clinopyroxene Fe-Mg exchange thermometer of Bishop (1980) has been applied to some high grade metabasites.

Two feldspar thermometry

At the highest grades studied the rocks contain both plagioclase and K feldspar. Solvus thermometry in the binary (albite-K feldspar) and in the ternary systems (albite-anorthite-K feldspar) has been considered respectively by Stormer (1975) and by Powell and Powell (1977). The

latter modified Stormer's thermometer for the affects of anorthite in plagioclase, but not for K feldspar in plagioclase. These calibrations have been criticised by Parsons and Brown (1981) as premature. However they do suggest a thermometer which may be used "faute de mieux". For the plagioclase compositions used in this study large errors are to be expected. Two feldspar thermometry is prone to resetting due to exsolution on cooling so it might be expected that calculated temperatures would be too low (Bohlen and Essene,1977).

6.3 GEOBAROMETRY

Thermodynamic data for selected geobarometers *are* shown in table 6.1.

Plagioclase-garnet-aluminosilicate-quartz

Pressures may be estimated using the reaction :

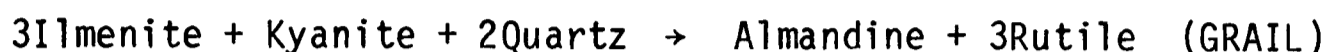


calibrated by Newton and Haselton (1981). The four component garnet model as described above has been employed as has the plagioclase activity model recommended by Newton and Perkins. This calibration gives considerably lower pressures than that employed previously by Wells and Richardson (1979) in the Dalradian. Likely alternative activity models might displace the calculated pressures by a few hundred bars. For instance assuming significant W_{FeMg} pressures will be reduced by a few hundred bars or using the plagioclase activity model of Saxena and Ribbe (1972) pressures will be increased by about 700 bars. The dataset of chapter 5 gives an expression for ALSIL reasonably close to the Newton and Haselton (1981) calibration. The dataset gives pressures about 0.5kb more than Newton and Haselton at 500°C and pressures about 0.4kb less than Newton and Haselton at 800°C. If compressibilities and expansivities are considered than pressures will be increased by a few hundred bars. Uncertainties in input mineral composition data give model errors of about

.6 to 1kb in addition to errors due to a possibly incorrect thermodynamic calibration.

Garnet-aluminosilicate-ilmenite-rutile-quartz

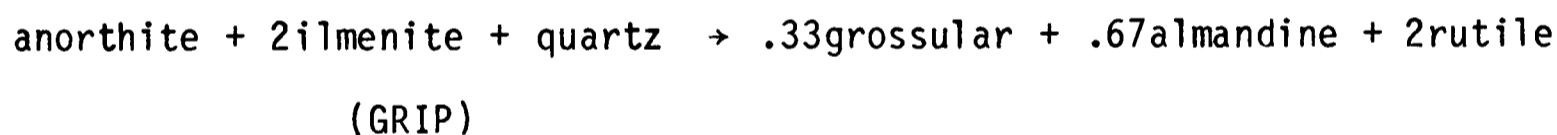
More recently the reaction



has been very tightly reversed (Bohlen et al., 1983a). Bohlen et al. suggested that a garnet solution model in which Fe-Mg interactions are significant ($W_{\text{FeMg}} \sim 2500 \text{ cal mol}^{-1}$) was necessary in order to make their barometer agree with the coexisting aluminosilicate polymorph in natural assemblages. Here no disagreement with the kyanite sillimanite equilibrium is apparent using the solution model described above. Model errors resulting from errors in input compositions of ilmenite and almandine are about .5kb to 1kb.

Garnet-plagioclase-ilmenite-rutile-quartz

The reaction :



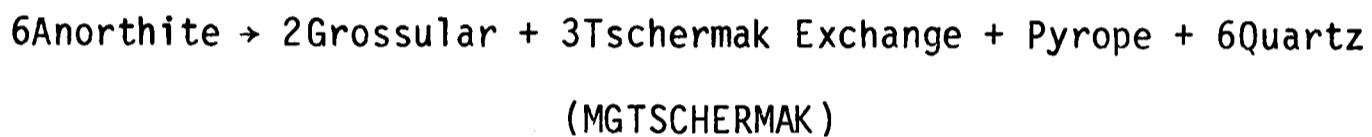
has been studied experimentally by Liotta and Bohlen (1984). The reaction as determined experimentally has a very steep slope and gives pressures far too low for the mineral compositions determined in this study. Furthermore the slope of this reaction is inconsistent with the slopes of the reactions ALSIL and GRAIL. Calculation of the reaction GRIP from the expression $(\text{ALSIL} - 2\text{GRAIL})/3$ results in pressure estimates in reasonable agreement with other barometers.

Plagioclase-garnet-muscovite-biotite-quartz

Ghent and Stout (1982) have discussed barometry in the assemblage plagioclase-muscovite-biotite-garnet-quartz. They presented an empirical calibration of the reaction:

3Anorthite + Annite → Grossular + Almandine + Muscovite (FEMICA)
 and for its Mg equivalent (MGMICA). For the reaction MGMICA thermodynamic data has been taken from chapter 5. Data for disordered phlogopite has been used. Pressures estimated from MGMICA using data for presumed ordered phlogopite gives pressures about 1.5kb lower than ALSIL. The reaction PHL (see chapter 5) applied to natural assemblages seems to suggest small errors in the dataset derived. However such small errors will result in small errors in resulting pressures owing to the large volume change of the reaction MGMICA.

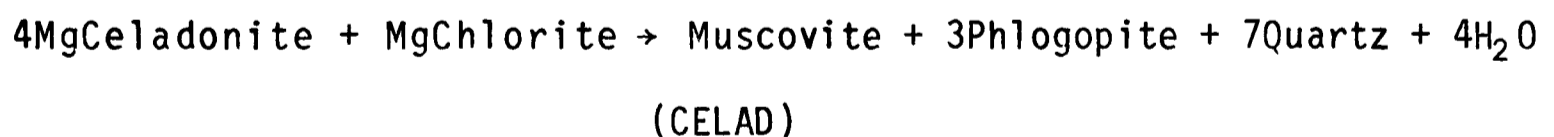
Another possibly pressure sensitive reaction is:



and its Fe equivalent FETSCHERMAK (Robinson, 1983). These reactions have and FEMICA have been used to constrain relative rather than absolute variations in pressure. The entropies and volume changes of reaction have been calculated from the data in table 6.2. Quoted pressures in tables are relative to an assumed pressure of 6.7kb in Glen Clova. Model errors are about 1kb from errors in input data.

Muscovite-biotite-chlorite-quartz

The reaction:



has been calibrated by an analysis of experimental phase relations in the system KMASH (Powell and Evans, 1983). In many of the rocks studied here chlorite is retrogressive after garnet. However a number of rocks contain chlorite within the schistosity apparently not related to the retrogressive breakdown of garnet. The thermodynamic data used by Powell and Evans (1983) are for presumed ordered phlogopite and for chlorite in an unknown state of order. If natural biotites are completely disordered

this would imply rather higher pressures. If the fluid was not entirely hydrous this would similarly imply higher pressures. Powell and Evans suggest that model errors are likely to be between 1 and 1.5kb. It is possible that chlorite is not an equilibrium phase in some of the rocks to which this reaction has been applied.

Plagioclase-garnet-clinopyroxene-quartz

The reaction:



has been calibrated using the best available enthalpy and entropy data (Newton and Perkins, 1982). It requires an empirical correction in order to make it consistent with the aluminosilicate phase diagram and with the orthopyroxene version of this reaction:



The barometer when corrected in this manner gives good agreement with other well constrained barometers (Ghent et al., 1983 ; Newton, 1983). Uncertainties in input data result in model errors of about 1kb.

Consistent geobarometry in the system CMAS requires the derivation of an internally consistent dataset for the various phases involved based on experimental phase equilibria. The reactions CPX and OPX as calculated from the self consistent dataset of chapter 5 yield pressures about 1kb lower than the Newton and Perkins (1982) calibration.

Plagioclase-clinopyroxene-quartz

In addition to the reactions described above the equilibrium:



has been used as a geobarometer in granulites. The equilibrium has been experimentally studied by Wood (1978). His data gives the equilibrium condition:

$$P=10.67T+20200$$

ΔV ($=-0.349$) is taken from Robie et al. (1978). Unfortunately the errors arising from the calculation of the activity of CaTs component in the clinopyroxene are considerable so that the barometer is of limited use, particularly as the clinopyroxenes in this study contain very low amounts of CaTs component.

Discussion

Bohlen et al. (1980) have criticised in general the use of exchange thermometers in high grade metamorphic terrains. In the Adirondacks they appear to give widely scattered results not related to progressive changes in metamorphic grade. It may be that exchange thermometry is not so useful in high grade areas which have been slowly uplifted (e.g. Barnicoat, 1983), but in more rapidly uplifted terrains this may not be so. The tendency of biotite to reequilibrate during cooling from high grades is well known. At higher temperatures as in the Glen Muick area where garnet biotite thermometer scatter is attributed to reequilibration. Alternative methods less prone to resetting such as garnet clinopyroxene exchange thermometry are obviously to be preferred. Similar problems will obviously occur with solvus thermometers.

It is hoped that reequilibration of barometers will be less widespread. This might be expected if the reactions involved are net transfers rather than exchange reactions and if cooling paths are subparallel to the slopes of geobarometrical equilibria. It is an assumption of the methods employed that all barometers and thermometers closed at the same temperature and pressure. It is hoped that this assumption is reasonable here although it will obviously sometimes not be so, particularly in high grade rocks (e.g. Fraser and Lawless, 1978).

A number of the geobarometers used here suffer from poorly constrained activity models for the phases plagioclase and garnet.

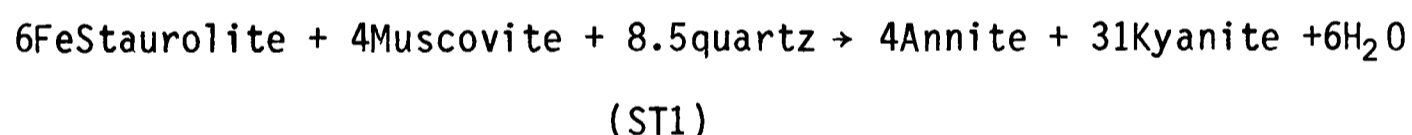
Relative errors in the pressures calculated are likely to be much less than absolute errors. The range of natural garnet and plagioclase compositions encountered is relatively small so that a changed activity model is likely to affect all pressures to a similar degree.

6.4 DEHYDRATION REACTIONS

Dehydration reactions may be used to constrain temperature making the assumption of regionally constant or smoothly varying fluid composition or to constrain the composition of the metamorphic fluid given pressure and temperature.

Reactions involving staurolite

A number of reactions involving staurolite will be discussed first as they have been used to constrain regional P-T variations in previous Dalradian syntheses. Biotite in the assemblage kyanite-staurolite-biotite becomes more ferroan with increasing grade. This change may be related to the reaction:



Harte and Hudson (1979) attempted to calibrate isopleths of 100Mg/(Fe+Mg) (M/FM) of biotite in this assemblage. They inferred a slope of relatively low dP/dT while Chinner (1980) suggested that the isopleths were almost isothermal within the kyanite field, but had a lower dP/dT within the andalusite field. The slope of this reaction has been estimated using more recent thermodynamic data (see table 6.2). Staurolite entropy has been estimated from Pigage and Greenwood's (1982) preferred value of ΔS (taking an average of their extreme values) for the reaction :



using their model D which assumes 2(OH) per staurolite molecule ($\text{Fe}_2\text{Al}_9\text{Si}_{3.75}\text{O}_{22}(\text{OH})_2$). This model is in accord with that of Yardley

(1981) and is necessary in order to reconcile the experiments of Rao and Johannes (1979) and Ganguly (1972).

Slopes of M/FM of biotite in A-S-B are very steep and positive within the kyanite field ($dP/dT \sim 750 \text{ bar}^\circ\text{C}^{-1}$) and smaller and positive within the andalusite field ($dP/dT \sim 45 \text{ bar}^\circ\text{C}^{-1}$). It is thus considered reasonable to treat the isopleths as isothermal within the kyanite field, in agreement with Chinner. Thermodynamic data are not sufficiently refined to calculate the position of the end member reaction relating to the isopleths, but it may be calibrated by reference to garnet-biotite temperatures as in figure 6.1.

The reaction ST2 has been used as a constraint on fluid compositions (e.g. Pigage and Greenwood, 1982). They found that using the 2(OH) staurolite model that estimated $a_{\text{H}_2\text{O}}$ was unbelievably low and suggested an error in the experimental work. The water contents of natural staurolites (Lonker, 1983) and their complex FeMg exchange behaviour with chloritoid (Grambling, 1982) suggests that the behaviour of staurolite may be quite complicated. 2(OH) per staurolite molecule lies in the middle of the range of OH contents of natural staurolites as determined by Lonker.

Paragonite dehydration

The reaction:



has been used to constrain metapelite fluid compositions (e.g. Pigage and Greenwood, 1982). Thermodynamic data for this reaction have been taken from Holland (1981b). High albite has been used as this gives values of $X_{\text{H}_2\text{O}}$ which are more reasonable (Pigage and Greenwood, 1982).

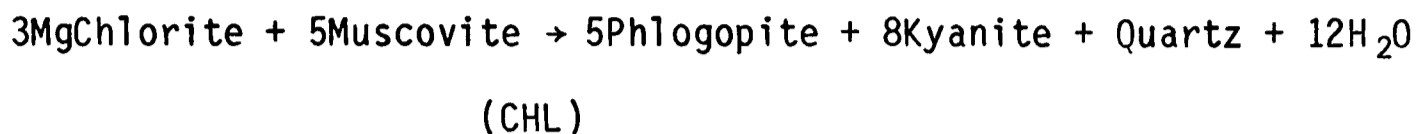
Muscovite dehydration

The reaction:



has been experimentally determined by Chatterjee and Johannes (1974).

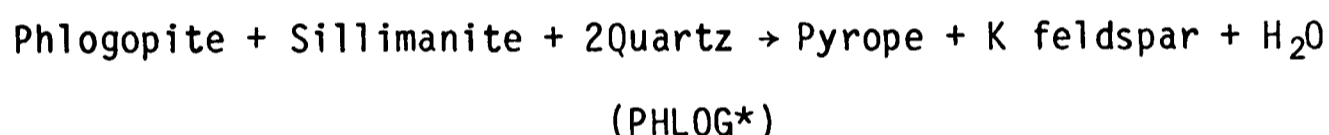
Chlorite-Kyanite-Phlogopite-Muscovite-Quartz



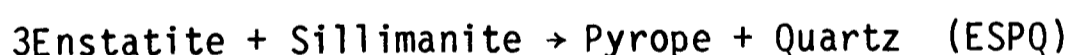
This reaction has been experimentally determined by Bird and Fawcett (1973). The position of the reaction has been calculated using the dataset of chapter 5 which is not consistent with the experimentally determined reaction. Data for ordered phlogopite were used. If disordered phlogopite data were used then the estimated proportion of water in the fluid would be increased. Use of this reaction to predict water activities is at present obviously subject to large uncertainties.

Garnet-Biotite-K feldspar-Sillimanite-Quartz

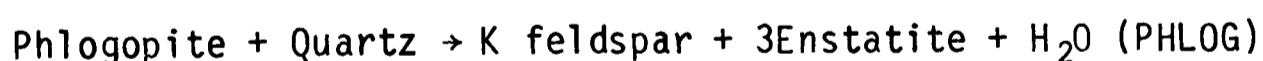
The reaction:



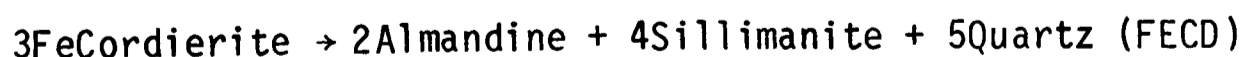
and its Fe equivalent ANN* may be used as water fugacity indicators. The Mg reaction has been used by Schmid and Wood (1976). They derived PHLOG* by addition of the reaction:



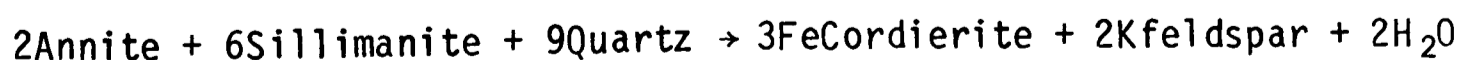
to the reaction:



However the latter as discussed above may not be well constrained. Alternatively the Fe end member reaction may be used as by Phillips (1980). He added the reaction:



as determined by Weisbrod (1973) and the reaction:



determined by Holdaway and Lee (1977). The result produces an expression for ANN* with an entropy inconsistent with tabulated entropies from the

literature (see table 6.4). The negative slope of the experimentally determined breakdown of FeCordierite to Almandine, sillimanite and quartz is in doubt. It is inconsistent with a positive slope for the Mg version of the reaction and the observed natural Fe-Mg exchange behaviour of garnet and cordierite (Lonker,1981; Martignole and Sisi,1981). In addition the correct model may not have been used to account for the presence of water in the channels of the cordierite molecule. It has been attempted to constrain the positions of these reactions by a study of experimental phase relations in the system CKMASHCO₂ (see chapter 5). Data used is for disordered phlogopite as ordered phlogopite data predicts X_{H_2O} greater than 1.0.

Hornblende Dehydration

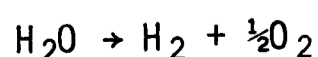
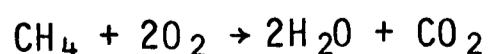
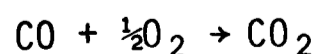
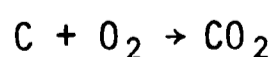
The reaction:



may be used to estimate water activities. This has been attempted by Percival (1983). Thermodynamic data is taken from the chapter 5 dataset.

6.5 FLUIDS IN EQUILIBRIUM WITH GRAPHITE

The compositions of fluids in equilibrium with graphite have been determined for rocks at the P-T conditions of a number of areas. Graphite is common in metapelitic schists in the Central Highlands-Glen Ey-Glen Avon areas. The fluid composition has been calculated using the methods of Ohmoto and Kerrick (1977) assuming all significant fluids are in the system C-O-H and $\sum P(\text{fluids}) = P_{\text{TOTAL}}$. Expressions for the equilibrium constants for the reactions:



have been taken from Ohmoto and Kerrick. Fugacity coefficients for water

are from Burnham et al. (1969), for CO₂ from Schmulovich and Shmonov (1975) and for H₂, CH₄ and CO from Ryzhenko and Volkov (1971). Ideal mixing of the fluids has been assumed to be a reasonable approximation for the purposes, following Ohmoto and Kerrick (1977).

6.6 MELTING REACTIONS

Percival (1983) has considered the vapour absent melting reaction:



(MELT)

as a constraint on the temperature of metamorphism. This reaction may be located approximately using the dehydration reaction



(HB)

calculated from data in Helgeson et al. (1978) and the melt producing reactions studied experimentally by Kilinc (1979):



(GRT)

assuming $a_{\text{H}_2\text{O}}^{\text{MELT}} = a_{\text{H}_2\text{O}}^{\text{FLUID}}$. Ideality of fluid mixing and ideal partitioning of vapour into the melt is assumed. The vapour absent melting reaction is located by the intersection of the melting reaction with the dehydration reaction at a given $a_{\text{H}_2\text{O}}$.

6.7 THE ALUMINOSILICATE PHASE DIAGRAM

The aluminosilicate phase diagram is an important potential constraint on the pressures and temperatures of metamorphism. The position of the triple point is the subject of controversy. It is placed at ~3.8kb and 500°C Holdaway (1971) or at 5.5kb and 620°C (Richardson et al., 1969). A possible discriminant between these two rival triple points is the experimental work at 1bar of Weill (1966) (in Holdaway, 1971) which favours a low pressure triple point (Day and Kumin, 1981). Day and Kumin

suggest a triple point of about 3.8kb and 500°C based on the data of Holdaway and of Weill or one of 4.8kb and 580°C based on the data of Richardson et al.. More recent work based on lattice vibrations also favours a low pressure triple point (Salje and Werneke,1982). Calorimetric entropy determinations on the three polymorphs are also indicative of a relatively low pressure triple point (Robie and Hemingway,1984). Assemblages diagnostic of a low pressure-temperature triple point have also been discovered, that is paragonite-sillimanite-quartz (Grambling,1984), chlorotoid-sillimanite-quartz and cordierite-kyanite (Holdaway,1978).

Thermobarometrical estimates of triple point conditions might be potentially used to discriminate between the two alternatives. However uncertainties in the barometrical calibrations preclude any definite statements. It may be stated that the barometrical calibrations employed here as tested in other terrains are consistent with a relatively low pressure triple point (Grambling,1981; Hodges and Spear,1982). Oxygen isotopes support a triple point temperature of about 500°C (Rumble,1978). Study of experimental petrogenetic grids reveals that many isograd reactions occur at temperatures too high by comparison with the low pressure-temperature triple point of Holdaway (e.g. Harte and Hudson,1979) although this discrepancy may be easily explained if $P_{H_2O} < P_{TOTAL}$. A triple point of about 4.0kb and 530°C is adopted as being consistent with the entropy data of Robie and Hemingway (1984), the recommendations of Day and Kumin(1982) and with the temperature estimates in this *thesis*.

The aluminosilicate phase diagram is used below as a constraint on regional pressure and temperature variations and as a check on the validity of the various thermodynamic calibrations employed. This might be considered unwise (Thompson,1976) as the aluminosilicate polymorphs

regularly persist metastably outside their stability field and there is even the possibility of their metastable growth (Hollister, 1969; Vernon, 1979). It is however assumed below that rocks containing two regional alsilicate polymorphs equilibrated somewhere near the appropriate phase boundary.

6.8 RESULTS

Calculated pressures and temperatures are shown in tables 6.5 through 6.18 and in figures 6.3 through 6.5. Results for individual rocks are shown in figures 6.6 through 6.14. It is emphasised that the P-T distributions shown in these figures are envisaged as being polychronic and in no sense represent an instantaneous picture of the regional P-T variations.

Temperature

The patterns of temperature variation deduced from biotite M/FM data and from exchange thermometry are comparable. The three exchange thermometers seem to agree reasonably with each other although the garnet amphibole temperatures scatter somewhat, perhaps due to variable f_{O_2} . Garnet-biotite temperatures by Ferry and Spear as modified by Hodges and Spear (table 6.3) range from about 540°C in the lower part of the kyanite zone (e.g. Glen Avon) to about 800°C in the sillimanite-K-feldspar zone (Glen Muick). Application of the Ganguly and Saxena modification yields slightly different results (table 6.4). The Ganguly and Saxena temperatures are in good agreement with a triple point at 530°C. The Glen Clunie estimates are reduced and in general estimates are more consistent with reasonable triple point estimates. Estimates are especially reduced for Mn and Ca poor garnets with relatively low Fe/Mg. This calibration may be more reasonable although it might be difficult to reconcile some dehydration reactions with it (see below).

Garnet clinopyroxene temperatures (table 6.6) range from about 720°C near the kyanite-sillimanite isograd (in the Duchray Hill Gneiss) to 800°C in the sillimanite-K feldspar zone in Glen Muick by the Ellis and Green method. The Ganguly and Saxena thermometers give results about 80°C higher than this. The empirical Dahl thermometer gives 650-730°C for the kyanite sillimanite isograd in the Duchray Hill Gneiss to 800°C to more than 900°C in Glen Muick which is not reasonable. The only reasonable calibration in this instance is that of Ellis and Green.

Garnet-amphibole temperatures (table 6.5) range from about 600°C in the middle kyanite zone (Schichallion area) to about 780°C in the sillimanite-K feldspar zone. Estimates of about 700°C are obtained for the area between Glens Clova, Esk and Muick. These estimates are all from Older Gabbro bodies of tholeiitic compositions. Garnet amphibole thermometry on other bulk rock compositions, for instance sedimentary derived amphibolites gives erratic and widely differing results. This presumably results from differing f_{O_2} or from complex activity composition relationships.

Ilmenite-clinopyroxene thermometry yields estimates of about 720°C for three Glen Muick rocks. However the thermometer is near the lower end of its possible application.

Various calibrations of the two feldspar thermometer give scattered results (table 6.7). The Stormer thermometer gives 750°C to 800°C, Powell and Powell 540°C to 600°C and Parsons and Brown 625°C to 775°C. The somewhat low temperatures of the preferred Parsons and Brown thermometer suggest that reequilibration may have occurred.

In the higher grade areas of Glens Esk, Clova, Muick and the Duchray Hill Gneiss some garnet-biotite temperatures appear to be anomalously low.

This may be attributed to retrograde Fe-Mg exchange. In some of the highest grade rocks in Glen Muick and Cromar there is more scatter in Fe/Mg ratios in garnets and biotites. Temperatures have been calculated using average biotite compositions away from garnet and average edge plateau compositions. Using extreme Fe/Mg ratios from garnets and biotites from a typical Glen Muick rock would give temperatures varying between 750°C and 850°C. Garnet-clinopyroxene temperatures have not been affected so much by such retrograde exchange and are considered to be better temperature estimates.

Temperatures in general are consistent with the maximum stability of staurolite+quartz (Rao and Johannes, 1979) and of muscovite+quartz (Chatterjee and Johannes, 1974) if $P_{H_2O} \sim P_{TOTAL}$. Experimental work on tholeiitic bulk compositions suggests that clinopyroxene begins to appear at temperatures of about 700°C (Spear, 1981). This is in agreement with the estimated first temperature of appearance from exchange thermometer reactions. Temperatures near the andalusite-kyanite isograd are somewhat higher than those appropriate to a lower temperature triple point using the Hodges and Spear modification, but closely approximate it using that of Ganguly and Saxena.

6.8.2 Pressure

Pressure estimates using the ALSIL equilibrium (table 6.8) are about 2-4kb lower than those previously presented by Wells and Richardson (1979). Calculated pressures range from about 6.5kb in the Glen Clova area to 9-10kb in the Central Highlands (Schichallion) area. Pressures in the Glen Ey and Glen Avon areas are about 7-8kb. In the Duchray Hill Gneiss pressures are about 6-8kb (some of this variation may be real) by CPX and ALSIL. High pressures of about 8kb are estimated for the Glen Muick area. Pressures calculated in Glen Muick by ALSIL appear to scatter

from about 7-10kb probably due to high errors resulting from very small grossular contents of the garnets. Estimates by CPX scatter much less. Supporting evidence for these high pressures comes from the whole rock experiments of Green and Ringwood (1967). They suggested that the assemblage garnet-clinopyroxene-quartz defines a high pressure subfacies of the granulite facies. Their experiments indicate that quartz tholeites of M/FM=40 (estimated whole rock composition of the Glen Muick mafic granulites) will develop this assemblage at a minimum of 7-8kb at 800°C.

The ALSIL pressure estimates in this paper are consistent with the experimentally determined kyanite-sillimanite equilibrium (Richardson et al., 1968) (see figure 6.15). Use of the Wells and Richardson calibration would increase pressures by 2-4 kb and thus make them inconsistent with this equilibrium. The CPX equilibrium also gives results close to the kyanite-sillimanite equilibrium for rocks close to the kyanite-sillimanite isograd (807 and 809). Estimates of pressures from the intersection of the kyanite-sillimanite equilibrium with exchange thermometer temperatures gives results in good agreement with other barometers.

The GRAIL reaction (table 6.9) gives results approximately consistent with the results from ALSIL although some estimates from the Schichallion area seem too low and those from Glen Clova too high by comparison with this reaction. There may be problems with nonideality of haematite-ilmenite solid solutions, the garnet activity model adopted or non equilibrium with opaque phases. It is difficult to obtain reliable analyses of ilmenite in some cases. Often there is a large excess of Fe or an excess of Ti indicating the presence of disseminated rutile. Petrographically it is often difficult to decide whether ilmenite is part of the equilibrium assemblage. It commonly occurs as finely disseminated

grains in or around the edges of biotites. This may be interpreted as the retrogressive exsolution of ilmenite from biotite. The small volume change of the reaction makes it particularly sensitive to errors in input data.

The reaction GRIP as calculated from thermodynamic data gives entirely reasonable results compared to other barometers (table 6.10). The CELAD reaction (table 6.11) appears to give reasonable estimates of pressure for most rocks although this is not so in all cases. It gives results of 6-7kb at 550°C at $P_{H_2O} \sim P_{TOTAL}$ for four rocks in the Glen Avon area. The presence of graphite suggests that the fluid was not entirely hydrous and that pressures may be expected to be a few hundred bars higher than indicated by these estimates. However it is not certain whether chlorite is in equilibrium with other phases in most samples.

Pressure estimates by MGMICA are in good agreement with those by ALSIL (see table 6.12). Use of the FEMICA, MGTSCHERMAK and FETSCHERMAK reactions (tables 6.13 & 6.14) to constrain relative variations in pressure predicts on the whole similar variations to those indicated by other barometers: that is for instance about 4kb between Glen Clova and the Schichallion area. Estimates imply a gradual increase in pressure to the SW : about 6kb in Glen Esk, 6.5kb in Glen Clova and the Duchray Hill Gneiss, 7kb in Glens Avon and Ey and 10kb in the Central Highlands (Schichallion). A summary of pressure estimates is presented in table 6.15 .

No inconsistency occurs between the relative pressure estimates for these mica barometers and data for the aluminosilicate polymorphs. Estimates made to agree with the kyanite-sillimanite equilibrium in Glen Clova are everywhere else consistent with the appropriate polymorph.

Estimates of about 4.5kb for the Cowhythe Gneiss by these methods is in good agreement with the estimates of Droop and Charnley (1984) and the likelihood that the Cowhythe Gneiss equilibrated at pressures close to the aluminosilicate polymorph triple point. Results from the TSCHERMAK barometers seem rather high relative to MICA barometers.

Results from the geobarometer CATS prove to scatter enormously from 10 to 18kb for rocks in Glen Muick and the Duchray Hill Gneiss. The barometer is obviously of no practical use in this instance.

In addition to the kyanite-sillimanite equilibrium a number of other geological constraints may be considered. Wells and Richardson (1979) reported the assemblage kyanite + zoisite + garnet + hornblende + plagioclase + biotite + quartz from the Central Highlands area. Kyanite + zoisite is a high pressure assemblage requiring $P > 8\text{kb}$ at $P_{\text{H}_2\text{O}} \sim P_{\text{TOTAL}}$ (Chatterjee and Froese, 1976). The complete assemblage is diagnostic of high pressures (see Selverstone et al. 1983).

Wells and Richardson report the assemblage garnet + kyanite + chlorite without staurolite or chloritoid from the Glen Avon area. This assemblage has been found to be quite common in that area. It was considered diagnostic of high pressures when interpreted in terms of a KFMASH petrogenetic grid. Pressures of about 8kb or more would be implied. This reasoning may be invalid for the following reasons:

(a) In many of the rocks examined from the Glen Avon area it is not certain that chlorite is in equilibrium with garnet and kyanite. It sometimes crosscuts the schistosity, sometimes lies within it (mimetic growth?) and very commonly replaces garnet.

(b) Garnets from this area contain significant spessartine and grossular component. Garnets may be stabilised by the presence of these components relative to the pure KFMASH system.

(c) The exact magnitude of the high pressures implied is not well constrained by slope calculations in the petrogenetic grid. The affect of reduced water activities may significantly alter the position of invariant points. Reduced water activities are implied by the presence of graphite and the calculations below.

The assemblage chloritoid+biotite (muscovite+quartz) is believed to be pressure diagnostic. The field of its stability is terminated at maximum pressures just above the kyanite andalusite equilibrium (Harte and Hudson,1979). It occurs in the E Dalradian near Stonehaven (facies series B and C of Harte and Hudson) and in a number of other localities. Those in the Central Highlands may be relatively early in the metamorphic development (Harte,1984). The termination of the regional chloritoid+biotite zone to the SW (Chinner,1967) is in agreement with the calculated increasing pressures in this direction.

A cordierite-out isograd lies somewhere within the sillimanite zone north of Deeside (Porteous,1973). This will of course be compositionally dependent. Cordierite is stable to the north; to the south garnet+sillimanite. This may reflect increasing pressures to the south. Prejudice suggests that cordierite out occurs at about 4-5kb. If pressures in Cromar-Glen Muick are appropriate to the aluminosilicate polymorph triple point it might be expected that cordierite would occur in either K feldspar or garnet absent assemblages which it does not.

The consistency of the pressure and temperature estimates with various positions of the aluminosilicate polymorph triple point will now be considered. Estimates of about 6kb in the Glen Esk area imply a triple point of less than this pressure. To the west of the Duchray Hill Gneiss low pressure estimates of ~5kb lie near the andalusite zone and estimates of 4.7kb in the Cowhythe Gneiss approximate triple point conditions.

Temperature data for areas lying astride the andalusite-kyanite isograd (without sillimanite) suggest triple point temperatures of 550°C to 600°C using the Hodges and Spear version or ca. 550°C or less using the Ganguly and Saxena modification.

6.8.3 RECENT BAROMETRIC WORK

Recent geobarometrical work on Dalradian rocks was presented at the Geological Society Dalradian Conference (September, 1983). A number of estimates of other authors are relevant to the data presented here. Moles (1983) estimated pressures of metamorphism in the Aberfeldy area (between the Duchray Hill Gneiss and Schichallion) and arrived at values of 7-9kb based on ALSIL, CELAD, sphalerite barometry and the reaction



Harte et al. (in press) presented data for the Eastern Highlands based on MGMICA, ALSIL and CELAD in broad agreement with the data presented here. Other estimates for the SW Highlands have been presented by Graham et al. (1983) for the reaction CELAD leading to estimates of about 10kb at about 500°C for an early event and about 6kb for a later retrograde event.

6.8.4 FLUID COMPOSITIONS

Fluids in equilibrium with graphite

The compositions of fluids in equilibrium with graphite have been determined for rocks with P-T conditions appropriate to a number of areas (figure 6.16). Kyanite schists in the lower part of the kyanite zone are typically graphitic. Fluid compositions vary considerably with oxygen fugacity. However it has been suggested that in graphitic schists subject to progressive metamorphism that the fluid composition will be buffered to the maximum H₂O value possible. If this is so X_{H₂O} contents of the fluid

should be in excess of 0.8. The rest of the fluid will be composed dominantly of methane and carbon dioxide.

Using the reaction ST2 (table 6.16) estimated water activities are relatively low. In the lower part of the kyanite zone in graphitic schists (Glen Avon and the Schichallion area) estimated water activities are low. $X_{\text{H}_2\text{O}} \sim 0.1$ to 0.5. In the higher part of the kyanite zone in Glen Clova estimates are about 0.8 if the preferred temperature estimate is adopted. These estimates are of course sensitive to temperature estimates. They will be discussed further below.

The reaction PARAG (table 6.17) gives results generally comparable with the reaction STAUR. There is likely to be some uncertainty in the calculation of paragonite activity coefficients. However even assuming that the activity of paragonite is equal to one water contents of the fluid are still considerably less than one in the graphitic schists of the low kyanite zone. In the high kyanite zone $X_{\text{H}_2\text{O}}$ approaches one.

The reaction CHL (table 6.18) predicts $X_{\text{H}_2\text{O}} < 0.3$ to 1.0 in the low kyanite zone (Glen Avon and the Central Highlands) assuming the chlorite to have been in equilibrium with other phases. Muscovite + quartz breakdown is consistent with the higher temperature estimates in the sillimanite muscovite zone if $X_{\text{H}_2\text{O}}$ is > 0.3 .

The equilibrium PHLOG* (table 6.19) may be used to predict water activities exactly. It gives estimates of 0.2 to 0.3 in the sillimanite K feldspar zone. The errors in the application of these equilibria must however be considerable.

The reaction HBL predicts extraordinarily low water activities very much less than 0.1. This is probably due to the low concentration of tremolite in the hornblendes under consideration. A similar problem was encountered by Phillips (1980) who attempted to calculate the activity of

tremolite in paragonitic hornblendes. In this instance an empirical activity coefficient of about 5 per molecule of tremolite predicts $X_{\text{H}_2\text{O}}$ of about 0.3 in agreement with PHLOG* for Glen Muick metabasites.

The position of the reaction MELT is shown in figure 6.17 using the empirical activity coefficient in the calculations. It suggests temperatures of 800°C at about 8kb in good agreement with the other methods used for geothermobarometry of Glen Muick metabasites. The calculations are however somewhat dependent upon the empirically constrained activities of tremolite in paragonitic hornblende. However it would seem difficult to estimate temperatures much less than 750°C by this method.

Some previous studies, notably Pigage and Greenwood (1982) have noted the very low water activities predicted by the equilibrium ST2. They noted that they were inconsistent with water activities predicted by PARAG and with fluid compositions in equilibrium with graphite in an internally buffered rock. In this study it appears that the models for the reactions STAUR and PARAG do predict similar water activities. In the higher grade areas, both predict water activities approaching unity while in the lower grade areas they predict values of about 0.5 or less. These values are for graphitic schists and contradict estimates for fluids in equilibrium with graphite in an internally buffered rock. It may be that fluids in the graphitic schists were generally not internally buffered.

Calculations of fluid compositions by these methods are obviously subject to many errors. If estimated temperatures are systematically too low then $X_{\text{H}_2\text{O}}$ will be underestimated. For the reaction PARAG a difference of 50°C in the temperature estimate will lead to a consequent error in $X_{\text{H}_2\text{O}}$ of 0.3 and for the reaction STAUR of about 0.5. If temperature estimates for the low kyanite zone were increased by about 50°C then fluid

compositions would be appropriate to the maximum possible $X_{\text{H}_2\text{O}}$ possible in graphitic schists. However an increase in temperatures at higher grades would lead to inconsistency with the dehydration reactions there (the maximum stability of staurolite + quartz). It might be suggested that temperatures are only underestimated in the graphitic schists owing to the vagaries of the thermometrical calibrations or of the garnet activity model. If temperature estimates were increased for low grade rocks then estimates would be produced inconsistent with the low temperature triple point favoured by experimental and mineralogical evidence (see above). Temperatures in Glen Avon, for instance, are apparently less than those appropriate to the alsilicate triple point. Retrogression is more likely to effect the higher temperature rather than the lower temperature zones.

Systematic underestimates of the activity of paragonite might result in the estimated proportion of water in the fluid being too low. The calculations have been tried using $a_{\text{PARAG}}=1$. The results still indicate considerably lower results than indicated by the graphite-fluid equilibria. If anything the activity model adopted for paragonite might be expected to overestimate its activity as it considers the mole fraction of paragonite where only a small number of possible components are considered. Reactions in NaASH are apparently well located as indicated by the self-consistent dataset of Holland (1979).

Suggestions that STAUUR underestimates water activities by a considerable amount do not appear to be supported by the present data. At the higher temperatures it predicts values approaching one. At the low temperature end of the scale it predicts values much less than one. It does not thus appear from this data that staurolite reactions are consistently in error (cf Pigage and Greenwood, 1982). It should be noted

that staurolite solid solutions are probably more complicated than recognised by the activity model and ideal formula used here (Grambling, 1982; Lonker, 1983).

Assuming no systematic errors in temperature estimates or the thermodynamic formulation of the dehydration reactions it can be concluded that :

- (1) $X_{\text{H}_2\text{O}}$ are ~ 0.4 to 0.6 in graphitic schists in the low kyanite zone.
- (2) In graphitic pelites water contents in the fluid have not been buffered to maximum values as suggested by Ohmoto and Kerrick (1977). It is implied that the rocks were not closed to external fluids.
- (3) The reaction PHLOG* suggests moderately low water activities in the sillimanite K feldspar zone.

Discussion

Other studies of fluid compositions in amphibolite facies metamorphic terrains suggest variable $X_{\text{H}_2\text{O}}$. Hodges and Spear (1982) predict values of as low as 0.1 to 0.3 from PARAG. Grambling (1981) estimates values as low as 0.4 to 0.6 using the Gibbs Method. Ferry (1981) estimates values of 0.24 to 0.71 for graphitic sulphide rich schists and suggested that they were infiltrated by a CH_4 - CO_2 - H_2O fluid. It appears that low water activities might be quite common in the lower amphibolite facies. In other instances high values of $X_{\text{H}_2\text{O}}$ are estimated (e.g. Mohr and Newton, 1983). The question of how low water activities might be produced is something of a problem. A source of CO_2 or CH_4 fluids is required.

6.9 CONCLUSIONS

A number of different geothermobarometrical methods have been applied to rocks from the eastern Dalradian. These have yielded results consistent with each other and with the kyanite sillimanite equilibrium. Fluid compositions in metapelites have been estimated from a number of

equilibria. They are somewhat subject to uncertainties, but it appears that fluids were water poor in rocks in the low kyanite zone and in the sillimanite K feldspar zone.

Temperatures range from 540°C in the low kyanite zone to 800°C in Glen Muick in the sillimanite-K feldspar zone. Pressures range from 10kb in the Central Highlands to 4-5kb near occurrences of andalusite. Relatively high pressures have been estimated for the Glen Muick area.

CHAPTER 7

REGIONAL VARIATIONS IN PRESSURE
AND TEMPERATURE

In this chapter the regional variations in pressure and temperature are discussed and compared to previous syntheses. The thermodynamic calibrations, used to derive the pressure and temperature estimates, have already been the subject of discussion in chapter 5. It is assumed that the estimated pressures and temperatures represent peak metamorphic conditions. It is emphasised that peak temperature conditions are likely to be strongly diachronous across the Dalradian. The pressure temperature reconstructions in the figures represent diachronous peak metamorphic conditions. The distribution of pressure and temperature deduced here is compared to previous syntheses.

A knowledge of the distribution of peak metamorphic pressure and temperature will provide constraints on Dalradian thermal evolution. A knowledge of the variation in pressure and temperature with respect to the structure will constrain the nature of syn and post metamorphic deformation. Locations mentioned in this chapter are shown in figure 7.1.

7.1 PATTERNS OF P-T VARIATION

The data presented in chapter 6 are summarised in figures 7.2 and 7.3. Local variations in the Glen Muick and Cromar areas have been discussed in chapter 3. In figure 7.4 the regional patterns of isotherms and isobars are shown, as interpreted from geological constraints in addition to the direct thermochemical estimates. These constraints include:

(a) The aluminosilicate polymorph phase diagram with a triple point of about 4kb and 530°C which is compatible with garnet biotite temperature estimates by the Ganguly and Saxena (1984) method.

(b) The stability of the AFM assemblage chloritoid-biotite indicating pressures no more than slightly above the andalusite kyanite equilibrium (Harte and Hudson (1979)). These occur in the Stonehaven area.

(c) The pelite petrogenetic grid of Harte and Hudson (1979) adjusted to agree with the lower P-T triple point preferred here.

The distributions of pressure shown are somewhat subjective as a number of different and possibly inconsistent geobarometrical constraints have been used. If a higher pressure triple point is adopted then baric gradients in the Braemar and Glen Muick areas will be reduced, but the form of isobars may be retained.

Pressures generally increase from E to W from Glen Esk to the Central Highlands (Schichallion area) from 5-6kb to about 10kb. Details are tabulated in table 7.1. In NE Scotland pressures have been calculated for the aureoles of the Newer Gabbros (Droop and Charnley, 1984), giving estimates of about 4-5kb. It is uncertain whether these pressures are also appropriate to the regional event or not. The Newer Gabbros and Buchan regional metamorphism are held by Fettes (1970) to be approximately coeval. However it is possible that high grade conditions might have been attained for some considerable period of time before Newer Gabbro intrusion.

Temperatures increase from the Highland Boundary Fault to an axis from the Duchray Hill Gneiss through Glen Muick to Cromar and then decrease to the west of this axis. Evidence for such a decrease comes from :

- (1) garnet biotite Ferry and Spear temperatures modified for garnet non ideality either by the method of Hodges and Spear (1982) or Ganguly and Saxena (1984).
- (2) M/FM of biotite in the AFM assemblage kyanite staurolite-biotite.
- (3) $\ln K_D$ s for Fe-Mg exchange between staurolite and biotite (chapter 2).

This axis may continue to the SW for an unknown distance and be analogous to the garnet spine of Cowal in the SW Highlands (see Chinner, 1978, figure 7.5). To the NE the axis appears to continue between Deeside and the Inzie Head Gneisses. A thermal high is also present centred on Portsoy on the Banff Coast. It is uncertain to what extent the Newer Gabbros are responsible for this thermal high. Ashworth (1975)

attributes the high grade rocks in the Cowhythe Gneiss to the intrusion of the Huntly-Portsoy Newer Gabbro and presumably a similar argument applies to the south around the Morven-Cabrach intrusion. However the grade of these areas with the Newer Gabbros "removed" is uncertain. It is possible that the high grade metamorphic imprint in the Cowhythe Gneiss is partly regional in origin. Hornfelses are only locally developed around the margins of the gabbros. Fettes (1970) has shown the very localised effects of the Newer Gabbros.

P/T generally increases from east to west from Glen Esk to the Central Highlands. In the Buchan area rocks record conditions of both lower pressure and higher temperature than in parts of the Central Highlands to the west.

It should be strongly emphasised that the P-T distributions shown in the figures are in no sense envisaged as an instantaneous picture. It is highly likely that the metamorphic imprint is strongly diachronous. The figures represent an attempt at a reconstruction of diachronous peak metamorphic conditions across the Dalradian.

To the west of Glen Muick and the Duchray Hill Gneiss the distribution of grade appears to be quite complex. Low pressure andalusite and chloritoid-biotite bearing (J. Treagus, pers. comm.) rocks occur between high pressure rocks (~8kb) in Glen Muick-Duchray Hill Gneiss and Glen Ey. There also appears to be a corresponding temperature low between these areas. On the Portsoy coast deformed fibrolite-K feldspar bearing migmatitic gneisses occur to the west of the Cowhythe Gneiss, interleaved with andalusite-kyanite schists (Read, 1922; J. Ashworth, pers. comm.). These complexities in the distribution of grade are to be expected in circumstances of dynamic metamorphism in which deformation spans the metamorphic peak. These areas do not coincide with the axes of major post metamorphic folds.

7.2 DISCUSSION OF PREVIOUS WORK

The first thermochemical estimates of pressure were those of Richardson and Powell (1976) who estimated conditions in the NW Dalradian of about 5.5kb at 550°C. The earliest regional survey of P-T conditions by thermochemical methods was that of Wells and Richardson (1979). As already noted these are 2-4kb in excess of the estimates presented here. Their pressures ranged from 8 to 12kb at an approximately constant temperature of 600°C. Such high pressures appeared to be difficult to reconcile with the location of the andalusite-kyanite isograd proposed by Chinner and Heseltine (1979) (Chinner, 1980). High pressures of 12kb in Glen Ey occurred very close to the isograd (Chinner, 1980). The very high apparent baric gradient implied by this juxtaposition is somewhat reduced by the present estimates, but is still considerable ($\sim 0.6 \text{ kb km}^{-1}$) if an aluminosilicate polymorph triple point of between 4 and 5kb is adopted. Lower pressures are calculated for the andalusite bearing area, supporting the presence of such a baric gradient.

Isogradic studies, pioneered by Chinner (1966) and more recently exemplified by Harte and Hudson (1979) and Chinner (1980) (see figures 7.5 and 7.6), have attempted to calibrate isopleths based on several reactions and hence to derive the regional pattern of isotherms and isobars. The latter two studies attempt this by considering the intersection of the andalusite-kyanite isograd with isopleths of M/FM of biotite in the AFM assemblage kyanite-staurolite-biotite. However, the andalusite-kyanite isograd does not appear in detail to follow the course suggested by Chinner and Heseltine (1979) and followed in these papers. The suggestion that the andalusite-kyanite isograd may never have existed within parts of the sillimanite zone (see chapter 4) would cast doubt on the derived isotherms and isobars. If the andalusite-kyanite isograd may be retained, although displaced, then it seems unlikely that it was contemporaneous

with M/FM isopleths in other parts of the Dalradian. Extrapolation of isopleths to meet the andalusite-kyanite isograd will not be useful if the two are significantly diachronous. The M/FM of biotites along the andalusite-kyanite isograd are presumably likely to correspond to the highest grade sillimanite zone conditions and not to the imposition of the isograd. There seems no reason to suppose that biotite M/FM s should be frozen in before peak metamorphic conditions. It does not seem valid to remove the sillimanite "overprint " any more than it is valid to remove any other zone from the regional picture. Extrapolation of isopleths across possible tectonic boundaries and across areas of potentially very diachronous metamorphism might misrepresent the pattern of P-T variations and oversimplify it. If major syn or post metamorphic slides are present variations may be sharp and or complex.

Chinner (1980) presented an elegant hypothesis for P-T variation along the Banff Coast and suggested that temperatures increased to the west of Portsoy. The work of Hudson (1980) shows that passing from east to west along the Banff Coast (along facies series E of Harte and Hudson, 1979) isopleths of M/FM of biotite in A-S-B are intersected from the higher temperature, higher entropy side in a sequence of prograde hydration (see figure 7.6). Note that this does not require increasing hydration during prograde metamorphism. The progressive hydration is probably apparent and rocks need not have reached their preserved metamorphic conditions along P-T paths corresponding to passage through lower grade zones. Chinner suggested that at the andalusite-kyanite isograd (at Portsoy) that the biotite M/FM isopleths are refracted to close to isothermal (rather than having a much shallower slope in the andalusite field) and were thereafter intersected from the more hydrated side.

Chinner's hypothesis requires M/FM of biotite to decrease to the west of Portsoy. The data presented here suggest otherwise. Limited biotite

M/FM data imply decreasing temperatures to the west of Portsoy. This conclusion is supported by some Fe-Mg exchange data for staurolite and biotite (see chapter 2). The stability of the assemblages muscovite calcite quartz and muscovite zoisite quartz along the coast to the west of Portsoy (Peacock et al. 1968) suggest temperatures below the aluminosilicate polymorph triple point at ca. 4kb. Some garnet-biotite temperatures exist for this area, but only for very Fe rich biotites and garnets which it may not be reasonable to compare with average pelitic compositions and which will be subject to large errors owing to the low Mg contents. Unfortunately the lithologies in this area do not contain many assemblages suitable for the estimation of temperature or diagnostic of any particular grade. However the AFM assemblage kyanite-staurolite-biotite indicates that the area is in the kyanite zone (cf. Atherton, 1977).

To the south in the Water of Ailnack and Glen Avon areas relatively low temperatures are implied by:

(1) garnet biotite thermometry. The Ganguly and Saxena calibration of the garnet biotite Fe-Mg exchange reaction suggests temperatures below the triple point. The calibration of Hodges and Spear (1982) suggests that temperatures approximate triple point conditions.

(2) by the zonal pattern. AFM garnet-chlorite assemblages (see chapter 2) occur in Glen Avon and the Water of Ailnack. The assemblages muscovite-calcite-quartz, muscovite-zoisite-quartz, muscovite-zoisite-calcite-quartz, zoisite-rutile-calcite-quartz and paragonite-quartz imply temperatures less than the aluminosilicate polymorph triple point. Further to the east the sillimanite zone is reached. To the west of the sillimanite zone first the andalusite zone and then the kyanite zone is reached. It is suggested that the preserved surface pressure temperature

path shown in figure 6.6 is found (assuming no complications owing to deformation at a later stage).

(3) by high biotite M/FMs in A-S-B.

(4) by staurolite biotite Fe Mg exchange (see chapter 2).

Taken together these data support a general decrease of temperature to the west. This decrease is only slight and is accompanied by increasing pressures. The data would also be compatible with a slight increase in temperature. The data presented here does not confirm the presence of the thermal anticline suggested by Chinner (1980).

To the south Glen Girnock is obviously at lower grade than Glen Muick (chapter 3). Glen Ey is at lower grade than Glen Girnock as evidenced by garnet biotite thermometry, the stability of margarite-quartz in Glen Ey and the M/FM of biotite, coexisting with kyanite and staurolite in Glen Girnock.

To the west of the Duchray Hill Gneiss temperatures fall, as indicated by the stability of paragonite-quartz and the M/FM of biotites in kyanite staurolite-biotite assemblages. Temperatures appear to rise again further to the west. Temperatures decrease generally to the west although there is this anomalously low grade area to the immediate west of the Duchray Hill Gneiss. One occurrence of the assemblage paragonite-quartz is documented from this area.

Another discrepancy occurs with the estimation of pressures in the Glen Muick area near the andalusite-kyanite isograd. High pressures are implied by thermochemical estimates while isogradic schemes imply pressures less than the aluminosilicate triple point. This problem has been resolved by recognising that andalusite in this area is late (see chapter 4). The form of isobars shown in figure 7.4 based on thermochemical estimates is preferred.

7.3 HIGH THERMAL AND BARIC GRADIENTS

Parts of the Dalradian are characterised by very high thermal and baric gradients. Harte and Hudson pointed out the very high thermal gradients in Barrow's zones (their facies series A and B); these are further emphasised by the discovery of very high temperature rocks to the north in Glen Muick. Instances of such high gradients also occur elsewhere.

In Glen Muick a very rapid transition occurs from sillimanite-K feldspar gneisses ($T \sim 800^\circ\text{C}$) to lower grade kyanite-staurolite schists ($T \sim 680^\circ\text{C}$) to the west in Glen Girnock (chapter 3). A similar rapid transition occurs to the northwest of the Duchray Hill Gneiss ($T \sim 700^\circ\text{C}$) to lower grade rocks to the northwest ($T \sim 550^\circ\text{C}$) and of uncertain zonal status. This rapid transition is evidenced by the close proximity of the biotite A-S-B $M/FM=60$ isopleth to the west (E. McLellan and G. Chinner, pers. comm.). To the NW rather high baric gradients appear to exist between the higher pressures of Glen Ey and the andalusite-kyanite isograd (see above).

On the Buchan Coast at Portsoy a rapid transition occurs from Cowhythe Gneiss ($T \sim 680-800^\circ\text{C}$) to lower grade andalusite-kyanite schists ($T \sim 550^\circ\text{C}$). The higher grade Cowhythe Gneiss might be related to heat from the Huntly-Portsoy Newer Gabbro (Ashworth, 1975). If this is so the western aureole is strongly attenuated by comparison with the eastern margin. A similar attenuated aureole occurs to the south adjacent to the western margin of the Morven- Cabrach Newer Gabbro (Allan, 1970). Attenuated aureoles are also present around some other Newer Gabbros and have been related to late shear zones (Ashcroft et al., 1984).

Very high thermal gradients or thermal discontinuities may be explained by high strain zones operating synchronous with or later than the metamorphic peak. In some cases these might be quite difficult to discern as later thermal adjustments may smooth out variation i.e. causing retrogression in the overthrust sheet while enhancing the grade of buried rocks. The occurrence of synmetamorphic slides is documented for the appropriate parts of the Dalradian (e.g. Coward, 1983a, Treagus and Roberts, 1981; Bradbury et al., 1979; J. Treagus pers. comm.). At Portsoy synmetamorphic movement occurred on the Portsoy Slide (Treagus and Roberts, 1981; Coward, 1983b). The operation of late shear zones in this area has also been postulated (Ashcroft et al., 1984).

Another possible explanation of these high thermal gradients is the operation of local heat sources as the result of magma intrusion. Magmatic heat sources of various ages abound within the Buchan area. The widespread high thermal gradients in Barrow's Zones appear to occur over too wide an area to be attributable to such a mechanism. Heat supplied from such a large source would presumably have an effect similar to that of the overthrusting of a thick crustal slice i.e. high thermal gradients would rapidly decay. Elsewhere, for instance in the Portsoy area high thermal gradients might be associated with the Newer Gabbros. However attenuation of the aureoles of these gabbros would seem to necessitate appeal to deformational processes.

Apparent high baric gradients between kyanite-andalusite isograd and the Central Highlands (preserved rather than actual) are not explainable in such terms. The ample evidence for syn and post metamorphic sliding, thrusting and shear zone formation suggests that these processes are responsible for the high thermal gradients, thermal discontinuities and complexities of isopleth distribution.

Very sharp thermal transitions and high thermal gradients appear to mark the western limit of the thermal high. The highest temperature rocks in the Dalradian appear to be separated from lower temperature rocks by sharp thermal transitions. This suggests the operation of deformational processes.

INVERTED ISOGRADS

No new data are presented bearing on the inversion of isograds, but the problems involved will be briefly reviewed. If the isograds are locally inverted this will have important consequences for tectonic models. Of particular interest is the orientation of isograds in Barrow's zones (facies series A of H&H). Tilley (1925) originally mapped the garnet isograd in the Central Highlands and concluded that it was inverted. More recently Chinner (1980) asserted that the kyanite isograd to the south of the Duchray Hill Gneiss was inverted on the basis of its displacement by the Fearnach Fault. Watkins (1984) has remapped the garnet isograd in the Central Highlands and deduced its inverted nature. This does not necessarily reflect a thermal inversion as the garnet isograd is compositionally dependent. In contrast Harte and Hudson believe that Barrow's zones are not inverted except possibly locally as the result of the formation of the late Highland Border Downbend. They associate the very high thermal gradients with a downward moving block within the Midland Valley. This would imply vertical movements in the Midland Valley synchronous with continued sliding (horizontal) movements in the Dalradian. The Highland Border Downbend may be associated with the formation of the Boundary Fault, but is much later than the metamorphism (e.g. Bradbury et al., 1979). If the downbend marks the initiation of such vertical movements it is too late to affect the thermal gradients of Barrow's Zones. Tectonic movements do appear to be required to explain the high gradients in Barrow's Zones but need not necessarily be vertical in

origin. Horizontal movements may be more plausible. If inverted gradients are present within the Barrovian Zones (and evidence seems to favour this) then their preservation requires long lived continuous deformation. If deformation was short lived or episodic these inverted gradients might decay.

If the existence of a Tarfside Nappe is regarded as accepted (Harte,1979), then it is clear that isograds crosscut early structures. Isograds are clearly continuous across the proposed boundary of the Tay and Tarfside Nappes. Any inverted isograds related to shear in the lower limb of the Tay Nappe must have moved as a result of later thermal relaxation, so that they now crosscut these early structures.

DISCUSSION

Harte and Hudson considered the form of isobars and attributed them to post metamorphic folding. This hypothesis appears to be quite reasonable in the Boyndie Bay (Banff Coast area) and for some distance southwards. Folding of the appropriate orientation has been identified. The Boyndie Syncline which was originally believed to be responsible for the present orientation of the P structures is now believed to be pre metamorphic (Treagus and Roberts,1981), but other late folding of similar orientation does exist and might be responsible.

Extension of this hypothesis to other areas appears to be less appropriate. Chinner (1978) considered the Boyndie Bay thermal trough to be continuous with one associated with the Loch Awe Syncline in the SW Highlands. This fold however is undoubtedly premetamorphic (Roberts and Treagus,1977). The axial trace of the Boyndie Syncline may be traced some way southwards (see data in Harte and Hudson,1979), but there is no evidence for its presence to the west of Glen Muick or to the west of the Morven-Cabrach Newer Gabbro.

Harte and Hudson associated their "P antiform" with a number of structures, the Buchan anticline, the Tarfside Culmination and parts of the Highland Border Downbend. High pressure rocks in Glen Muick, Cromar and the Duchray Hill Gneiss are not associated with any such post metamorphic fold nor are the high pressure rocks in the Central Highlands. The P structures postulated by Harte and Hudson (1979) would have a large amplitude (as evidenced by the fact that they deform isobars from 2-6kb) and seem an unlikely style of deformation.

A more dynamic interpretation of pressure variations is preferred. Pressure variations may be produced by other processes apart from post metamorphic folding. Wells (1979) has modelled pressure variations in the Central Highlands by a process of concurrent erosion and heating after crustal thickening with varying initial depths of burial or variable erosion rates. "P structures" might also be associated with thrusting rather than folding events, particularly as there is much evidence for synmetamorphic thrusting. Preserved isobars are likely to be diachronous (England and Richardson, 1977; chapter 1) as has been demonstrated for the Dalradian case in particular by Dempster (1984). If this is so there will be no simple relationship between isobars and postmetamorphic folding. It is not possible to assume (as do apparently Harte and Hudson) that isobars are everywhere synchronous. If isograds are inverted within the Tay Nappe then certainly some explanation other than postmetamorphic folding must be sought (Chinner, 1980). It is concluded that, while post metamorphic folding in the type Buchan area is an adequate explanation for the distribution of isobars, the simple version of this hypothesis is inappropriate elsewhere.

If simple post metamorphic folding is to be rejected to explain the thermal high in the Glen Muick-Duchray Hill Gneiss area then some other

explanation must be sought. It may be that a local heat source was responsible. Alternatively it may be explained by a tectonic hypothesis. Sliding may have emplaced high temperature over low temperature rocks.

7.6 TECTONOTHERMAL MODELS

The observed distribution of pressure and temperature in the Dalradian is believed to be attributable to both post metamorphic deformation, the nature of synmetamorphic evolution and the amount of extra heat input to a given area from the mantle. To understand the observed distribution of pressure and temperature tectonic models must be formulated. Regional variation in P/T may be considered with respect to a number of simple tectonothermal models:

(a) crustal thickening by continental overthrusting followed by heating concurrent with erosion.

(b) crustal thickening by vertical stretching followed by heating concurrent with erosion.

(c) heating as a result of thermal input from below.

(d) crustal stretching.

The first two possibilities have been modelled by England and Richardson (1977) and England and Thompson (1984). They differ merely in the means of achieving the required crustal thicknesses; by the overthrusting of one unit of crustal thickness or by a progressive restacking of the crust with a more homogeneous distribution of strain. The observed thermal effects are similar and will produce P-T paths in which pressures initially decrease as temperatures increase. According to England and Thompson (1984) only high pressure amphibolite or blueschist facies conditions will result.

They suggested that some other form of tectonothermal process was necessary to account for the presence of andalusite-sillimanite facies series; heat input, crustal stretching or the tectonic uplift of

kyanite-sillimanite facies series rocks inducing rapid erosion. Heat input might occur as a result of magma intrusion, infiltration by fluids which might be an important contribution to crustal heat budgets (Etheridge et al., 1983 cf. England and Thompson, 1984). Alternatively one could invoke a higher heat flow from the mantle, perhaps as a result of the juxtaposition of hot asthenosphere with cool crust consequent on crustal shortening (Houseman and MacKenzie, 1981) or as the result of crustal stretching.

Rocks in the Central Highlands have been modelled by a process of concurrent heating and erosion after crustal thickening (Wells, 1979). The appropriateness of such a model is supported by the high pressures estimated for Central Highlands rocks coupled with the evidence that crustal thicknesses are at present no less than average (Bamford et al., 1979). The occurrence of Buchan metamorphism as the result of heating not dependent upon crustal thickening is suggested by the generalised models of England and Thompson (1984) and possibly also by the shape of Buchan facies series (see below) assuming these facies series to be of the sort modelled by England and Richardson (1977).

Harte and Hudson (1979) considered that most Buchan facies series approximated the shape of normal geotherms. They attempted to estimate the magnitude of vertical metamorphic gradients in the E Dalradian, that is those perpendicular to isobars rather than those on the present ground surface. They concluded that, except adjacent to the Highland Boundary Fault, these gradients were relatively low and, coupled with average surface to depth gradients implied by estimated metamorphic conditions, indicated P-T profiles strongly convex towards the P axis. The estimation of these gradients is somewhat subjective as the orientation of isobars and isotherms below the present ground surface is unknown. Harte and Hudson's diagrams were based on smooth variations with depth. The details of their synthesis may in any case be disputed as the slopes of their

biotite M/FM isopleths are believed to be vertical in the kyanite field. However facies series do definitely appear to be convex towards the temperature axis along the Buchan Coast where some reactions are intersected from the higher temperature higher entropy side in a sequence of apparent prograde hydration (Hudson,1980).

Such steep profiles might be expected if cooling was isobaric rather accompanied by decreasing pressures. This state of affairs would be expected if heating was without significant crustal thickening (England and Richardson,1977). It is tentatively concluded that the Central Highlands area was metamorphosed as the result of tectonic thickening while the Buchan area attained its metamorphic conditions as the result of the addition of heat to the crust. Areas such as the Duchray Hill Gneiss, Glen Clova and Glen Esk may have achieved their metamorphic conditions through a combination of these two mechanisms. Further evidence on this problem is presented and discussed in the chapter on P-T evolution.

CONCLUSIONS

Previous attempts at the delimitation of the regional distribution of isotherms and isobars have been modified in the light of new data. A high temperature axis is recognised coinciding with the Duchray Hill Gneiss-Glen Muick area. In particular, high pressures are asserted for an area astride the former andalusite-kyanite isograd, and temperatures are believed to decrease consistently to the west of the sillimanite zone. High thermal and perhaps high baric gradients are present in the Dalradian and may be explained by syn or postmetamorphic sliding. At its NW margin the high temperature axis is marked by a very sharp thermal transition to lower grade rocks. The present orientation of isobars is only in part attributed to post metamorphic folding in the Buchan area. Elsewhere the variations in pressure may be related to syn or post metamorphic

deformational events, or to regionally variable erosion rates or thicknesses of initial cover.

In NE Scotland low P/T metamorphism is attributed to a high heat flow environment possibly related to a continental margin arc (Yardley and Senior, 1982). In the Central and SW Highlands metamorphism occurred by tectonic thickening in the absence of extra heat flow. Rocks in the Glen Esk-Glen Clova areas may have been metamorphosed by a combination of the two mechanisms.

CHAPTER 8

PRESSURE TEMPERATURE EVOLUTION

Evidence from the Dalradian will now be used with a view to constraining the pressure-temperature evolution of the crust during the Grampian Orogeny. This evidence will comprise recorded mineral zoning profiles and evidence for various mineral reactions. Data recorded previously in the literature will be discussed.

8.1 ALUMINOSILICATE POLYMORPH RELATIONSHIPS

Aluminosilicate polymorph relationships have been discussed in chapter 3. The relationships will now be considered from the point of view of P-T evolution. In the northern Buchan area, at least in Newer Gabbro aureoles there is evidence for the reaction andalusite \rightarrow sillimanite which presumably reflects increasing temperature. To the west of the Buchan area andalusite is replaced by kyanite suggesting an increase in pressure during the metamorphic evolution (assuming the replacement not to have been retrograde). In the Glen Muick, Glen Clova and Glen Esk areas kyanite is replaced by sillimanite. This might be the result of pressure fall, temperature increase or retrograde processes during falling pressure. Chinner (1966) has advocated an isobaric temperature rise model while Wells (1979) has suggested that uplift may have been occurring. If any of the andalusite in the Glen Muick Cromar areas is of regional origin then the sequence kyanite \rightarrow sillimanite \rightarrow andalusite implies decreasing pressures. Chinner and Heseltine (1979) report kyanite replaced by regional (?) andalusite from eastern Deeside which be compatible with decreasing pressures (or if kyanite grew at temperatures below the aluminosilicate polymorph triple point, with increasing temperatures)

In summary the reactions occurring between the different polymorphs imply:

- (1) a probable near isobaric heating path for parts of the Buchan area.
- (2) a pressure increase at some stage during the metamorphic evolution, in areas to the west of the Buchan area.

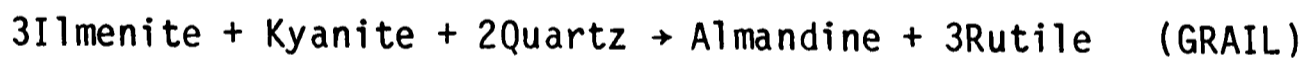
(3) pressure decrease in the southern part of the sillimanite zone if the andalusite along Deeside is regional. If the andalusite is all of thermal origin then it is not possible to distinguish between the Chinner isobaric and the Wells isothermal origins for sillimanite. Further evidence is required as the overprinting relationships of the aluminosilicate polymorphs are ambiguous.

8.2 Early Chloritoid Biotite

Harte et al.(1984) report an early AFM chloritoid biotite assemblage from the Central Highlands. This must reflect pressures no more than just above the andalusite-kyanite equilibrium (Harte and Hudson,1979). High pressures are in contrast recorded by equilibria among garnet and plagioclase which reflect a later stage in the metamorphic evolution. This must reflect an increase in pressure during metamorphism as suggested by Harte et al. (1984).

8.3 Rutile and Ilmenite

Recently the reaction :



has been experimentally determined by Bohlen et al. (1983a). The reaction is almost isobaric with almandine and rutile being stable at the higher pressures. A number of rocks contain the phases rutile and ilmenite, coexisting with garnet, kyanite and quartz. Some contain ilmenite throughout the rock, but with rutile present only as inclusions in garnet. This suggests the operation of the reaction GRAIL from right to left which would indicate a decrease in pressure. However, it is possible that continuous reactions involving garnet might also lead to the disappearance of rutile. For instance an increase in the activity of almandine might result in the progress of the reaction from right to left. However, in the assemblages considered (AFM kyanite-garnet-biotite) such an increase is, itself, only likely to result from a decrease in pressure (see diagrams of

Spear and Selverstone, 1983). On the basis of these observations decreasing pressures are suggested for the Cromar (919D & 966D), Duchray Hill Gneiss (637D) and Glen Clova (135A, 155, 131A, 141A) areas.

8.4 Plagioclase-garnet retrograde equilibria

Some rocks from higher grade areas in Glen Clova and the Duchray Hill Gneiss show both zoned garnet and plagioclase. The garnet zoning profiles (see the appendix) are interpreted as the result of peak metamorphic homogenisation, followed by retrograde reactions at the rims during uplift. In rocks 141, 155, 129A and 637D rims are depleted in grossular, while adjacent plagioclases are zoned to increasing anorthite contents near the edges (figure 8.1). This type of zoning in the AFM assemblage kyanite-garnet-biotite is interpreted as the result of the operation of continuous reactions such as ALSIL and MG & FEMICA. Increasing almandine and decreasing grossular contents of the garnet rims probably indicate decreasing pressures and temperatures. These zoning profiles are treated quantitatively below.

The following reaction relationships are found in Glen Clova rocks:

- (1) the reaction of kyanite to fibrolite.
- (2) continuous reactions, resulting in garnet and plagioclase zoning profiles.
- (3) evidence of reactions resulting in the appearance of ilmenite and the disappearance of rutile.
- (4) in rock 135B late staurolite has overgrown trails of fibrolite.

It is possible that all these reactions represent the same segment of the pressure-temperature path, along which the rock evolved. Together they suggest decreasing pressures after peak metamorphism and the growth of sillimanite during uplift and cooling. Alternatively the different

reactions for which evidence is preserved may represent different segments of the P-T path.

8.5 Reactions in Garnet Amphibolites

Garnet amphibolites may be expected to preserve traces of earlier assemblages and reactions better than metapelites owing to their greater resistance to deformation and the fact that they often require hydration during prograde metamorphism, limiting possible reaction.

There is petrographic evidence in garnet amphibolites of reactions involving garnet resorption. The textures are discussed briefly in chapter 2. Garnets are replaced by plagioclase, zoisite or occasionally by calcite. The textures which provide evidence of these reactions are only preserved in amphibolites which show little trace of deformation. No rigorous treatment of the reactions leading to garnet resorption may be performed owing to the high variance of the assemblages involved (generally garnet-plagioclase-quartz-hornblende-opaques). However it is likely that reactions involving garnet resorption are pressure sensitive with garnet being developed at high pressures. Most reactions in simplified systems involving garnet resorption in this assemblage are very pressure sensitive. It seems likely that garnet resorption does reflect decreasing pressures. Rocks showing these textures are found in the Central Highlands and in Glen Esk (see chapter 2).

8.6 QUANTITATIVE P-T PATHS FROM ZONING PROFILES

Recently a quantitative method for the calculation of P-T paths from zoning profiles has been presented by Spear and Selverstone (1983). It involves the solution of a set of linear equations comprising:

(1) a Gibbs Duhem equation for each phase.

$$0 = \bar{S}dT - \bar{V}dP + \sum x_j d\mu_j$$

(2) the condition for heterogenous equilibrium:

$$0 = \sum v_i \mu_i$$

where a linearly independent set of reactions are chosen so as to fully characterise the system.

(3) a set of equations introducing derivatives of compositional terms of the form: $0 = -(d\mu_2 - d\mu_1) - (\bar{S}_2 - \bar{S}_1)dT + (\bar{V}_2 - \bar{V}_1)dP + \frac{\partial^2 \bar{G}}{\partial X_2^2} dX_2$

for a binary solution where \bar{S}_i and \bar{V}_i are partial molar quantities. Additional cross derivatives of \bar{G} are introduced for ternary or higher order solid solutions. These equations are chosen according to the phases and components of interest. Terms in these equations are calculated following Spear and Selverstone (1983). Ideal mixing was assumed. The dataset of Spear and Selverstone (1983) (which follows in most part Helgeson et al. (1978) was employed). The resulting set of linear equations is solved by matrix methods using the program in the appendix. As the partial differentials of pressure, temperature and composition with respect to composition are functions of pressure, temperature and composition the set of linear equations must be solved iteratively for small steps of pressure, temperature and composition.

Critique

The technique is a very valuable and powerful one. However it may be difficult to use for a number of reasons. It takes account only of continuous reactions among phases of interest. It is likely that many of the rocks studied will have undergone discontinuous reactions since the initial growth of garnet and that these will be recorded in the zoning profile. From this point of view it would seem best to apply the method to assemblages which are stable over considerable pressure temperature ranges, making the occurrence of discontinuous reactions less likely e.g. garnet amphibolites.

The method may also be applied to retrogressive zoning profiles. However in this instance problems may arise with variable closure of different reactions. For instance, if garnet biotite exchange continues for some time after pressure sensitive net transfer reactions, then derived pressure temperature paths are likely to be erroneous. In many instances analytical errors may introduce considerable errors into calculated P-T paths.

Application

This method has been applied to zoning profiles of garnet at high grade in the AFM assemblage garnet-kyanite-biotite. Results are tabulated in table 8.1 and figure 8.2. Zoning profiles in rocks from the southern sillimanite zone in Glen Clova and the Duchray Hill Gneiss all indicate decreasing pressure during evolution. This was accompanied by slight increases or decreases in temperature.

The shapes of the P-T paths, indicated in figure 8.2 for assemblages with kyanite would be altered if sillimanite was assumed to be the aluminosilicate polymorph present, during creation of the garnet zoning profile. Trial calculations indicate that possible P-t paths range from isobaric with $\Delta T \sim +100^\circ\text{C}$ from core to rim (change in anorthite content from core to rim $\sim +0.05$) to paths with $\Delta T \sim -40^\circ\text{C}$ and $\Delta P \sim -0.5\text{kb}$ from core to rim (with anorthite contents in plagioclase decreasing by about 0.05 from core to rim). It is assumed that kyanite is the stable polymorph during evolution of the zoning profile on account of:

(1) not all the rocks contain fibrolite. 637D does not contain fibrolite. 141A contains little fibrolite. All rocks contain large and abundant kyanites.

(2) the rocks studied lie very close to the kyanite sillimanite isograd. P-T conditions would only just have reached those appropriate to

sillimanite growth and hence most of the zoning profiles would be expected to represent equilibrium with kyanite. It is concluded that rocks in the southern part of the sillimanite zone developed sillimanite mainly as the result of decreasing pressures.

Preliminary attempts have been made to apply this method to similar assemblages (some also with staurolite) in rocks from the Central Highlands and Glen Avon. Results have ranged from decompression paths with little temperature variation to paths showing increasing pressure and temperature. Application of the method is limited by the expectation that many zoning profiles resulted from discontinuous reactions and that garnets are not likely to have been in equilibrium with porphyroblast phases throughout the period of their growth. Many of the rocks used gave unreal results, in that calculated compositions of various phases became negative along the calculated P-T paths.

8.7 CONDITIONS OF CONTACT METAMORPHISM

If pressures in the thermal aureoles of dated intrusions may be estimated and earlier regional metamorphic conditions are known average uplift rates may be constrained. Contact metamorphic pressures have been estimated with a small number of samples for:

(1) hornfelses around Newer Granites and Newer Diorites in the Glen Muick area.

(2) hornfelses close to the Haddo House Newer Gabbro.

These estimates will provide further P-T-t points for the evolution of the eastern Dalradian. Other estimates already exist for most of the other Newer Gabbros (Droop and Charnley, 1984; Leslie, 1984) and for other Newer Granites in the Dalradian and Moine (Wells and Richardson, 1979; Droop and Treloar, 1981; Ashworth and Tyler, 1982; Tyler and Ashworth, 1983) (see table 8.2).

A number of geothermobarometrical methods will be used in addition to those used in the earlier part of this chapter. These will be introduced in the next few sections.

Garnet-Quartz-Plagioclase-Wollastonite

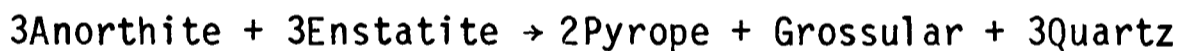
The assemblage garnet-plagioclase wollastonite occurs in some contact metalimestones in the Pollagach Burn (NN407943). These must lie to the low temperature side of the reaction:



owing to the absence of quartz. This reaction has been experimentally determined by Newton (1966), Boettcher (1970) and Windom and Boettcher (1976). The line $P=25.5T(^{\circ}\text{C})-13,300$ describes the equilibrium (Droop and Treloar (1981). In this instance ideal mixing on sites activity models have been employed.

Plagioclase-Garnet-Orthopyroxene-Quartz

The reaction:



(MGOPX)

and its Fe equivalent FEOPX are useful geobarometers. MGOPX has been calibrated by Newton and Perkins (1982) on the basis of the best entropy and enthalpy data. FEOPX has been determined from experimental data by Bohlen et al. (1983b). Both reactions are satisfactory in that they agree with the aluminosilicate phase diagram. MGOPX has been estimated using the data of chapter 5.

Garnet-Cordierite

A number of empirical calibrations exist for the Fe-Mg exchange behaviour of garnet and cordierite. The calibration of Holdaway and Lee (1977) has been employed here.

Garnet-Orthopyroxene

Fe-Mg exchange between garnet and orthopyroxene has been experimentally calibrated by Harley (1984) as a geothermometer. The Al content of enstatite in equilibrium with garnet has been experimentally calibrated as a barometer for use at high pressures (Harley and Green, 1983). At lower pressures the slope of this reaction makes it useful as a geothermometer.

Reactions involving Cordierite

A number of cordierite bearing reactions are useful geobarometers. Unfortunately there is much debate about the role of water in the cordierite structure as a factor causing its stabilisation to higher pressures. Newton and Wood (1979) treated cordierite as a solid solution between MgCordierite and hydrous MgCordierite. Martignole and Sisi (1981) treated the presence of water in cordierite as reflecting the operation of a physical equilibrium and predicted a greater stabilisation of cordierite than the Newton and Wood model. More recently Ellis (in preparation) has found that for some reactions the water content of the fluid does not effect the position of reactions or the M/FM of cordierite involved except under totally anhydrous conditions.

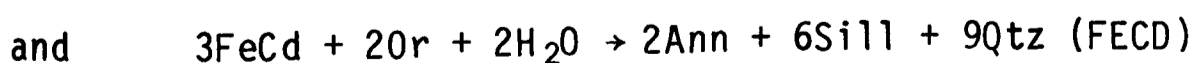
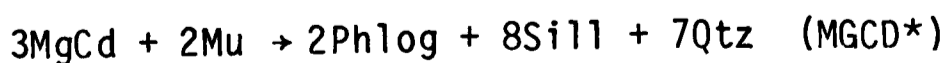
Reactions around an invariant point in MAS(H) may be considered involving the phases cordierite, pyrope, sillimanite, enstatite and quartz. Limited data exists for this system. Expressions for the anhydrous reactions may be calculated from the data in table 8.2. The reaction (PY) lies at about 6.2kb at 800°C slightly lower than the position suggested by Newton (1972). In the hydrous system this reaction is located at 11.2kb at 800°C (Newton, 1972). Cordierite must be stabilised by the addition of water to the cordierite structure. The model of Newton and Wood (1979) fails to produce the required amount of stabilisation, while that of

Martignole and Sisi (1981) is closer. The calculations of Lonker (1981) are also not consistent with the amount of stabilisation required. An activity coefficient for Mg Cordierite in hydrous Mg cordierite at 11kb and 800°C in a hydrous fluid of about 0.07 is implied by the calculations. Assuming a similar γ_{MgCd} for the reaction (EN) which lies at similar pressures to

(PYR) at 800°C a pressure for equilibrium of 11.3kb is obtained. This is consistent with the stable breakdown of cordierite to talc, kyanite and quartz (see Lonker, 1981).

Application of these reactions to lower pressure rocks is complicated by the unknown activity of cordierite in hydrous cordierite under these conditions. The reactions may be calculated with reasonable confidence in the anhydrous system, but a cordierite model is required for the hydrous system. The Newton and Wood (1979) and Lonker (1981) models have already been rejected at higher pressures (see Lonker, 1981). The Martignole and Sisi (1981) model is not in agreement with the work of Ellis and requires an independent estimate of the water activity. It is known that cordierite contains less water at low than at high pressure. Hence it might be expected that the activity coefficient of cordierite in hydrous cordierite would be less at low pressure than at high pressure. Conditions calculated in the anhydrous system and in the hydrous system with the estimated 11kb, 800°C activity coefficient probably bracket the real conditions at $P < 11\text{kb}$ and $T \sim 800^\circ\text{C}$.

Other pressure sensitive reactions exist which it may be useful to consider :



The first has been experimentally determined by Seifert (1970) and the latter by Holdaway and Lee (1977). The reactions have been assumed to have

end member locations as estimated by Droop and Treloar (1981). The pressure change resulting from calculations involving natural compositions is given by :

$$\Delta P = -RT \ln K / (\Delta V_s + nV_{H_2O})$$

where the volume of water under given conditions is from Burnham et al. (1969). Differences from experimental conditions are relatively small. It is assumed that the volume of water is constant over the pressure range considered and that the activity coefficient of cordierite is constant. The Fe equivalent of (ENST) has

been experimentally determined (Weisbrod, 1973; Holdaway and Lee, 1977) and may also be used. However the negative slope of this reaction is in doubt as it is inconsistent with a positive slope for (ENST) and the observed natural Fe-Mg partitioning between garnet and cordierite (Lonker, 1981; Martignole and Sisi, 1981).

RESULTS

Newer Diorites and Granites

Results are shown in table 8.3 for rocks from the aureoles of the Lochnagar Newer Diorite (GM3AZ-N0315822), the Lochnagar Newer Granite (IN1-the west side of Leac Gorm around N0220955), and the Kincardine Granite (583C-NN407943). Pressures by MGOPX, FEOPX and by SILL are 2kb in good agreement with each other. Garnet-biotite, garnet-cordierite and garnet orthopyroxene reactions indicate a temperature of 800°C or above, but this of course has only local significance. In the aureole of the Kincardine Granite the occurrence of the assemblage garnet-plagioclase-wollastonite constrains pressures to be less than the reaction WOLL. The occurrence of andalusite not sillimanite in hornfelses adjacent to these rocks constrains pressures to be less than 3.4kb. Reactions FECD and MGCD* suggest pressures of about 2kb for rock IN1 from the Lochnagar

Granite Aureole. The reaction FECD requires pressures to be less than 4.5kb for the rocks from the Newer Diorite aureole.

These pressures were achieved at 415 ± 9 Ma, the date of the intrusion of the Lochnagar Newer Granite (Halliday et al., 1979). If peak metamorphic pressures of about 8kb were achieved before 515Ma this implies an uplift rate of 0.1 to 0.2 kmMa^{-1} .

These results may be compared with those from the aureoles of other Scottish Granites (table 8.4). These data imply an average uplift rate in the 100Ma or so after metamorphism of about 0.15 kmMa^{-1} somewhat less than the figure suggested by Wells and Richardson (1979). The cordierite barometers used by these authors are probably in error.

The pressures recorded from the Lochnagar and Etive aureoles are somewhat less than those implied from the Foyers aureole to the northwest although they are of similar age. Watson (1964) noted the fact that aureoles to the northwest are not so distinct suggesting the observation that regional temperatures to the northwest were higher at 400Ma. These higher regional temperatures and the small amount of post 400Ma differential uplift are compatible with later metamorphism, cooling and isostatic readjustment in areas towards the northwest.

Newer Gabbros

Hornfelses have been investigated from part of the aureole of the Haddo House Gabbro (see Read, 1952) (606A-NJ922310). Conditions calculated by FEOPX, MGOPX and SILL average about 3.2kb (table 8.5) at about 800°C . This pressure may be slightly less than that appropriate to the Morven Cabrach and Huntly-Portsoy Newer Gabbros ~ 4.5 kb (Droop and Charnley, 1984). Slightly lower pressures of 3.5kb are hinted at for the Inch Gabbro (Leslie, 1984). However such a suggestion cannot be established as the pressure difference is equivalent to the errors in the calculations.

The fairly similar pressures for all Newer Gabbro intrusions indicates that they were all intruded at approximately the same level. Droop and Charnley (1984) conclude that no tilting of NE Scotland has occurred since this time. However if all gabbros were intruded at the same level and they were then folded and tilted this conclusion does not necessarily hold.

The Newer Gabbro pressure estimates may be compared with the slightly lower pressures of 2-3kb estimated for the Buchan Zones (Hudson,1984) which is reasonable considering their higher structural level.

Summary

Pressures in the aureole of the Lochnagar Newer Intrusions are about 2kb. These pressures, attained at 415Ma indicate uplift rates of .1 to .2 kmMa⁻¹ averaged over the first 100Ma after peak metamorphism. These uplift rates compare with those estimated from other Newer Granite Intrusions.

Estimated pressures in the aureole of the Haddo House Gabbro are about 3.2kb. These are within error of pressures calculated for other Newer Gabbro intrusions.

8.8 DISCUSSION

The P-T paths suggested for different areas are indicated in figure 8.3. These P-T paths may be related to various tectonothermal models which were discussed in chapter 7. In the Buchan area isobaric or near isobaric heating may be related to heating in the absence of great tectonic thickening.

In the southern sillimanite zone there is evidence that sillimanite grew under decreasing pressures. Evolution under decreasing pressures suggests that tectonic thickening may have been a significant influence in the thermal evolution of this area. This is, of course, not an unreasonable conclusion in an area characterised by nappe tectonics. The

distinction between the Buchan near isobaric heating path and the south sillimanite zone near isothermal path emphasises the different evolution of the two areas and the likely diachroneity of metamorphism between the two areas.

In the Central Highlands there is evidence of early tectonic thickening. This is attributed to continuing crustal thickening throughout most of the thermal evolution. Later evolution must have involved decreasing pressure in order to accomplish the required differential uplift relative to the Buchan area by 400Ma. Resorption of garnets in garnet amphibolites may reflect this uplift. It seems unlikely that maximum temperatures would be reached during increasing pressures in the absence of heat input or special tectonic circumstances.

8.9 CONCLUSIONS

- (1) In the Buchan area heating was approximately isobaric.
- (2) In the south sillimanite zone pressures decreased during the growth of sillimanite.
- (3) In the Central Highlands limited evidence indicates that pressures were increasing until a relatively late stage in the thermal evolution (at least locally). Pressures then must have decreased.
- (4) Pressures in dated Newer Granite contact aureoles indicate that uplift rates, averaged over the first 100Ma after peak metamorphism were 0.1 to 0.2mmyr^{-1} . this probably reflects tectonic and isostatic uplift. The rough equivalence of contact metamorphic pressures at about 400Ma indicates that most differential uplift must have been accomplished by then.

CHAPTER 9

EVIDENCE FOR HIGH PRESSURE
METAMORPHISM IN THE MOINE

The Grampian Moines comprise an area which is geologically relatively unknown. Recent work has separated a high grade basement, metamorphosed at kyanite-sillimanite grade (Central Highland Division) (figure 9.1) from a cover metamorphosed under lower amphibolite facies conditions. It has been suggested that the Central Highlands Division represents Grenvillian basement while the Grampian Division was first metamorphosed during a postulated Moravian Orogenic Event at 750Ma. Later Caledonian reworking is known to have occurred (Piasecki,1980).

Unfortunately, therefore, the age of metamorphic assemblages in the area is open to speculation. Previous petrological work has been carried out by Winchester (1974) and Wells (1979). The former mapped mineral zones on the basis of assemblages in calcsilicates of given $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. Much of the Central Highlands lies within his clinopyroxene zone which he associated with the sillimanite zone in metapelitic rocks. However his methods lack rigour (see Wells,1983). Wells attempted to estimate pressures of metamorphism using assemblages in metabasites and concluded that pressures were high and well within the kyanite field. However, his thermodynamic methods were based on poorly constrained reactions and involved amphiboles for which activity models are not constrained. His barometers do not give reasonable results when applied to metabasites from areas with well characterised metamorphic conditions. Much of the area has certainly experienced sillimanite zone conditions and has undergone extensive migmatization (Ashworth,1979a; Piasecki,1980).

A garnet-clinopyroxene paragenesis reported in the early literature (Hinxman and Anderson,1915) has been investigated. It occurs from within the Central Highland Division about 4km south of Tomatin (Grid Reference NH792252, see figure 9.1). A small metabasite body about 100m long occurs infolded with migmatized gneisses containing the assemblage fibrolitic

sillimanite-K feldspar. Garnet-clinopyroxene assemblages are preserved preferentially within the centre of this body.

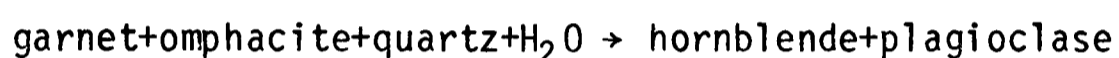
PETROGRAPHY

The metabasites contain the assemblage garnet-hornblende-plagioclase ilmenite-sphene-quartz-diopsidic clinopyroxene-apatite. Epidote, clinozoisite, biotite and retrogressive blue green amphibole also occur occasionally. A typical mode of a relatively unretrogressed sample is hornblende 59%, plagioclase 15%, diopsidic clinopyroxene in symplectitic intergrowth with plagioclase 18%, garnet 5%, quartz 2%, others 1%. Textures are illustrated in figures 9.2 through 9.4.

The clinopyroxene is present as a symplectitic intergrowth with plagioclase, interpreted as indicating the presence of an original omphacitic clinopyroxene (e.g. Mysen and Griffin, 1973). In most rocks studied this symplectite is absent and has been replaced by hornblende. Initial replacement of the symplectites occurs by the growth of very small hornblendes. Later growth and recrystallisation then occurs so that symplectites are eventually replaced by single large hornblendes. Sometimes larger hornblendes within symplectites are sieved by vermicular inclusions of plagioclase. Garnets are surrounded by coronas of plagioclase intergrown with minor hornblende. Large hornblendes always separate garnets and their coronas from remnant symplectite. Quartz occurs in most rocks, but generally not in plagioclase-hornblende coronas around garnet. If not elsewhere it is sometimes preserved as inclusions within garnet. In some rocks (see figure 9.4) the quartz is separated from garnet by a reaction rim of hornblende. Similar reaction rims of hornblende may occur between quartz and symplectite. Ilmenite occurs close to garnets and in areas formerly occupied by garnets which have now been totally resorbed. Sphene occurs as inclusions within hornblende and within the

clinopyroxene-plagioclase symplectites. Ilmenite is commonly rimmed by sphene, particularly when not in the close vicinity of a garnet. Biotite, epidote and blue green hornblende are late phases occupying the centres of spherical areas of hornblende-plagioclase intergrowth that have replaced garnet. Zoisite occurs sometimes as inclusions within garnet.

The textures present, the diopside-plagioclase symplectites and garnets rimmed by plagioclase coronas are typical of those occurring in many retrogressed eclogites (e.g. Mysen and Griffin, 1973; DeWit and Strong, 1975; Droop, 1983) and are consistent with the operation of a multivariant eclogite \rightarrow amphibolite reaction of the form:



is occurring.

9.2 CHEMICAL MINERALOGY

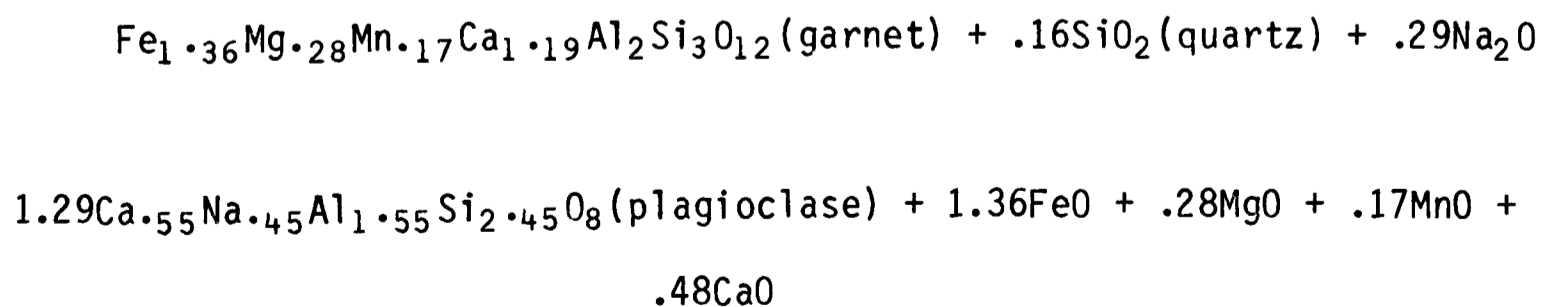
Representative analyses are given in tables 9.1a and 9.1b. Garnets have zoning profiles with decreasing grossular and spessartine and increasing pyrope to the rim (figure 9.6). Centre compositions are about $\text{Almandine}_{4.5}\text{Pyrope}_9\text{Grossular}_{3.8}\text{Spessartine}_8$. Clinopyroxenes are typically $\text{diopside}_{70}\text{hedenbergite}_{2.8}\text{jadeite}_2$ although more jadeitic pyroxenes do occur occasionally (up to $\text{jadeite}_{1.2}$). Defocussed microprobe scans of plagioclase-clinopyroxene symplectites have been carried out in order to calculate the composition of the original omphacite. ZAF corrections have been repeated in order to account for the fact that nearest neighbour interactions in a mineral of homogeneous composition are different from those in a mixture of phases of the same aggregate composition. The reintegrated analysis (table 9.1c) contains less than 4 cations per six oxygens and not enough sodium to balance aluminium. If it is assumed that sodium loss has occurred and the percent jadeite in omphacite is estimated

from the amount of aluminium then a composition of about Jadeite₃₅Hedenbergite₂₂Diopside₄₃ is suggested. Plagioclase compositions are very variable. Those within garnet coronas have compositions from anorthite₅₀ to anorthite₆₀ while those within symplectites average about anorthite₄₀. Recrystallised plagioclases outside garnet coronas vary from about anorthite₃₂ to anorthite₃₉. Hornblendes within garnet coronas have relatively low M/FM (~45) and high Mn and Al contents. Those within symplectites have high M/FM (~64) and low Mn and Al. Larger hornblendes resulting from the recrystallisation of finer symplectite hornblendes usually have intermediate, but variable M/FM (~50) and Mn and Al contents indistinguishable from those of corona hornblendes. Large recrystallised hornblendes are zoned in decreasing Na and tetrahedral Al. Their zoning in M/FM is variable, lower than centres when edges are near garnet and higher than centres when edges are near symplectite.

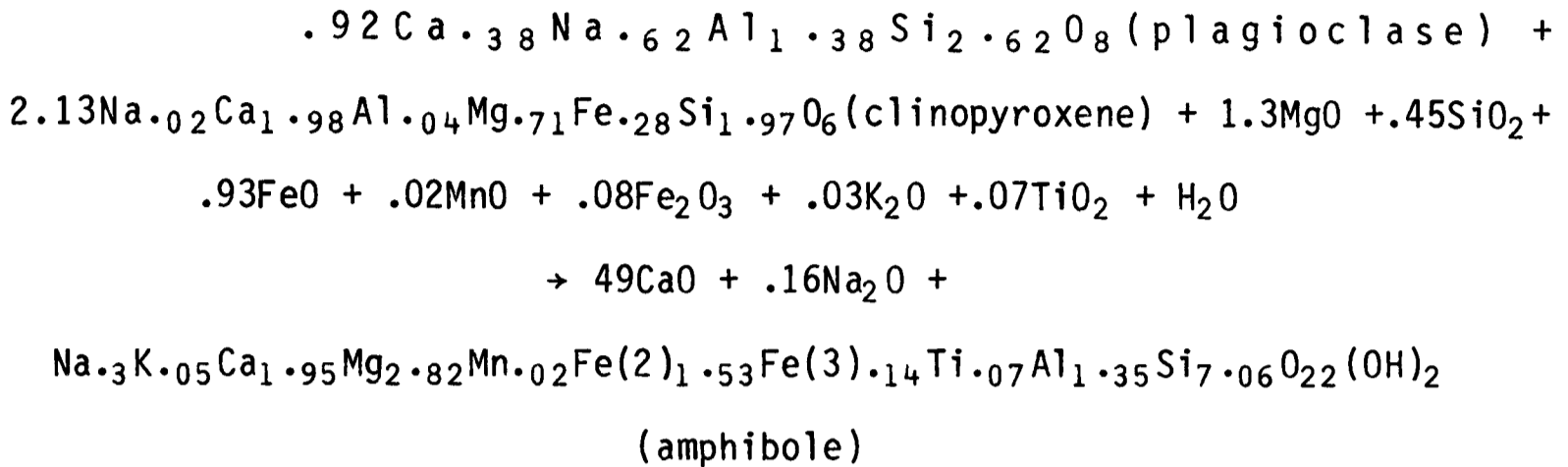
9.3 REACTION MODEL

The relative movements of the different components and the reactions occurring during amphibolitisation have been considered. The reactions derived will depend on the reference frame adopted (Gresens, 1967), commonly selected as one of constant Al or Si (e.g. Mongkoltip and Ashworth, 1983).

The assumption of Al immobility has been used to derive a reaction for the replacement of garnet by plagioclase (neglecting minor amphibole):



A similar calculation has been performed for the replacement of symplectite by "average" hornblende:



Reaction of eclogite to amphibolite has been achieved by coupled reactions occurring at two sites, around garnets and in symplectites. Various components diffused between these sites. Na diffused from symplectite to garnet corona and Fe, Mg and Mn from garnet to symplectite. Both reactions appear to have consumed quartz and water will of course also have been required. The calculations are necessarily rather crude and inaccurate, but are in agreement with petrographic observations viz.:

(a) hornblende reaction rims between quartz and garnet corona and absence of quartz from the corona.

(b) hornblende reaction rims between quartz and symplectite.

Consumption of quartz during these reactions indicates that the eclogitic assemblage garnet-omphacite-quartz was once present, a conclusion supported by the quartz inclusions in garnet.

The compositional variations in the product phases plagioclase and hornblende indicate the presence of chemical potential gradients on the scale of <1mm in the rock during amphibolitisation. Grain boundary diffusion between sites of reaction was the rate limiting factor during reaction rather than intracrystalline diffusion or rates of surface reaction (cf. Loomis, 1977). As a result of this slow grain boundary diffusion, hornblendes are richer in Ca, Mn and Al near garnets relative

to symplectites. Coronas are typical structures controlled by intergranular diffusion (Fisher, 1978).

Grain boundary diffusion may have been inhibited by lack of H_2O . Significant quantities of intergranular H_2O would be likely to produce fairly rapid grain boundary diffusion and consequent reaction (Ahrens and Schubert, 1975), particularly at the temperatures appropriate to the presence of sillimanite in surrounding rocks. The eclogitic assemblage is clearly not cofacial with sillimanite bearing assemblages in the surrounding migmatitic gneisses. The metastable persistence of such high grade relics in metabasites has been discussed by Heinrich (1983). Metabasite eclogites require the introduction of H_2O in order to achieve conversion to amphibolite facies assemblages while metapelitic rocks will undergo dehydration along the same P-T path. If diffusion of H_2O from metapelites to metabasites is sufficiently slow then high pressure metastable relics may be preserved in metabasites. Such a factor seems to have been involved in the persistence of eclogites described here. Melting and consequent buffering of the fluid composition to low a_{H_2O} in the surrounding rocks may also have been a factor as might be the fact that the rocks have been through several metamorphic cycles and will therefore be less hydrous. Such preferential persistence of high pressure rocks in metabasites explains why they are not cofacial with surrounding metapelites and why hypotheses of eclogite introduction from the mantle are not always required (cf. Lappin and Smith, 1978). The fact that reaction in the Tomatin Eclogite during amphibolitisation was inhibited by a probable lack of water is entirely consistent with such an hypothesis.

The following sequence of events is inferred. On uplift after the initial eclogite forming event diopside-plagioclase symplectites were produced from original omphacite. A later influx of water resulted in the

growth of hornblende and plagioclase. As the rock dried up and sites of reaction became increasingly separated by reaction products further reaction was inhibited.

9.4 EXTENT OF ECLOGITIC PARAGENESIS

Another amphibolite specimen collected in another part of the Moines (Laggan Bridge, NN57909273, see figure 9.1) shows remarkable textural similarities to the rocks described above although it contains no clinopyroxene. It contains the assemblage garnet-hornblende-plagioclase-ilmenite-sphene-quartz. Garnets are surrounded by plagioclase-hornblende coronas without quartz and are sometimes totally resorbed. Quartz is abundant, but is always separated from garnet coronas by a reaction rim of hornblende. Hornblende contains inclusions of plagioclase and sphene similar to textures of hornblende replacing symplectite in the Tomatin eclogitic amphibolite. It is suggested that this rock also contained the assemblage garnet-omphacite-quartz. Garnets rimmed by plagioclase-hornblende coronas are also described by Piasecki (1980) from this area. Eclogitic assemblages were probably present throughout this area at one time, but are now only rarely preserved. It is also interesting to compare these amphibolites with textures in some amphibolites of Dalradian origin, described in chapter 2.

9.5 AGE

The Central Highland Division in which these retrogressed eclogites have been found was subject to a number of orogenic events (Piasecki, 1980). The Central Highland Division is correlated by Piasecki with the Glenfinnan Division of the northern Moines for which a Grenvillian age is established. Syntectonic pegmatites occur from the area which give dates between 718Ma and 573Ma. These are interpreted as Moravian dates partially reset as a result of the Grampian Orogeny (Piasecki and vanBreemen, 1979). The plagioclase-rimmed garnets described by

Piasecki are held to have grown synchronous with the emplacement of these pegmatites. If these garnets are analagous to those in the Tomatin metabasites then the eclogites would be interpretable as Morarian in age.

A number of Piasecki's conclusions have been questioned. His correlation of the Central Highland and Glenfinnan Divisions used to infer a Grenvillian age for the former has been challenged (Roberts and Harris,1983). The syntectonic nature of the ca.750Ma pegmatites has been challenged in another area and the reality of a Morarian orogenic event questioned (Powell et al.,1983). In the light of these uncertainties a Grampian age might also be possible.

These eclogites might be compared with others from the Caledonide-Appalachian belt in Newfoundland, described by DeWit and Strong (1975). These are in an analogous structural position to those described here, from the basement structurally below units suggested to equate with the Dalradian. They occur in dykes which when they pass into the cover only contain amphibolite facies assemblages. DeWit and Strong suggested that this was because the dry conditions of the basement were required in order to initiate eclogite formation. The interpretation of this study would be that the lack of water favoured their preservation within the basement rather than in the wetter cover. An anhydrous environment is not necessarily required for eclogite formation (Holland,1979).

9.6 CONCLUSIONS

A former apparently extensive eclogitic paragenesis of garnet-omphacite-quartz has been recognised within the Central Highland Division of the Grampian Moines. Progradation to lower pressure amphibolite assemblages was inhibited by the slow intergranular diffusion of components between reaction sites, probably as a result of lack of sufficient intergranular water.

CHAPTER 10

A TECTONOTHERMAL MODEL
FOR DALRADIAN EVOLUTION

In this chapter, models of Dalradian structural evolution will be considered and an attempt will be made to explain the observed pattern of metamorphism in terms of them. Locations mentioned in the text are shown in figure 10.1.

10.1 THE CENTRAL HIGHLANDS

A number of models have been published in recent years for the Dalradian of the Central and SW Highlands. These have been briefly reviewed in chapter 1. Structural models which suggest the expulsion of nappes of opposing vergence from a central root zone steep belt are not followed in this discussion. The change in facing direction across the Tummel Steep Belt is not believed to be a primary feature.

The dominant vergence of structures in the Grampian Orogeny is towards the northwest (see for example Coward (1983a)). The Tay Nappe has a vergence opposed to this and might be viewed as an early backthrust nappe. The studies of Bradbury et al. (1979) and Roberts and Treagus (1979) among others have shown that in the Central Highlands early SE facing nappes such as the Tay Nappe were followed by later NW facing nappes and slides. These NW directed slides carried the Tay Nappe flat belt up to the northwest over the lower parts of the Dalradian stratigraphy. It will be assumed in what follows that this pattern of early southeast directed and later northwest directed sliding is applicable over the whole of the Dalradian. The more controversial structural setting of the northeast part of the Dalradian will now be discussed.

10.2 NE SCOTLAND

In the Buchan area the stratigraphy is the right way up, but in the lower limb of the Tay Nappe it is inverted. This observation has led to the proposal that the area comprised an equivalent to the now eroded upper limb of the Tay Nappe to the southwest. Read (1955) identified a slide

(lag) within this upper limb, the Boyne Line, along which, he believed, elements of the stratigraphy were excised (figure 10.2). This thrust sheet above the Boyne Line was termed the Banff Nappe.

More recently, Ramsay and Sturt (1979) have revived the concept of the Banff Nappe. They differ from most other workers in that they believe that the Rb-Sr whole rock isochrons of Sturt et al. (1977) indicate that the area is a slice of Precambrian basement. As discussed in chapters 1 and 3 this does not appear to be established. Ramsay and Sturt equate the base of their nappe with the Portsoy Thrust which lies to the west of Read's Boyne Line. The southern limit of their nappe coincides with a zone above the Deeside Limestone (figure 10.3).

If the Banff Nappe is part of the upper limb of a southeast facing recumbent fold then it might be expected that early smaller scale structures would be SE facing and recumbent. This is not always the case. On the Banff Coast the earliest structures face upwards (Treagus and Roberts, 1981). In the E some structures are westwards facing, while in the SE some folds are SE facing and recumbent (Read and Farquhar, 1956). Along Deeside the Deeside Limestone is inverted (Read, 1928a) indicating that early structures here are recumbent. The observations are consistent with the oncoming of SE facing recumbent structures as one proceeds southwards out of the Buchan area. The right-way-up Buchan stratigraphy must be separated from inverted Tay Nappe stratigraphy by a slide(s) or fold nappe closure(s) of presently unknown position (along the line A-B ? in figure 10.5). The stratigraphy may be correlated through the Glen Muick area from the Banff Nappe to the Tay Nappe (chapter 2).

The Banff coast section through Portsoy (see figures 10.5 and 10.11) is characterised by a series of early upright folds which face consistently upwards. A broad primary (local D1) synclinal structure, the Boyndie Syncline, exists to the east of Portsoy, complementary to the

Buchan Anticline further to the southeast (Treagus and Roberts,1981). This structure has been modified and steepened at its western edge by later monoclinial (D3) folding. Local D2 folds related to NW sliding (Coward,1983a) are found at the deeper structural levels, particularly around Portsoy.

Shear Zones

Of particular interest is the recent discovery of a set of relatively late regional amphibolite facies shear zones in NE Scotland (Ashcroft et al.,1984; see figure 10.4). These have been located by geophysical and by borehole work and are apparently of steep orientation. They contain high grade assemblages, similar to those in adjacent regional metamorphic rocks (Kneller and Leslie, 1984). They are in part associated with the Newer Gabbros; they deform and cause dismemberment of these bodies (e.g. Ashcroft and Munro,1978). They also deform some of the earlier ca. 470Ma acid intrusives. It is uncertain how these shear zones relate to other late phases of deformation.

10.3 THE BANFF NAPPE

The relationship of the Buchan (Banff) area to the surrounding areas is a matter for discussion. Ashcroft et al. (1984) have suggested that the area is essentially autochthonous, but has suffered differential vertical uplift on the steep shear zones mentioned above. In this interpretation crustal thickening in areas outside the Buchan terrain would have been achieved by a series of overthrust nappes which did not cover the Buchan area.

Alternatively, the Buchan area may be regarded as a major overthrust nappe (the Banff Nappe), allochthonous on areas now exposed to the NW and SE (Ramsay and Sturt,1979). Given that the Buchan area represents the highest overall structural levels present, it is possible that a nappe, containing rocks stratigraphically and metamorphically equivalent to those

in the Buchan area (now eroded away), once formed a major part of the tectonic overburden of these more northwesterly and southeasterly areas.

The Buchan area is bounded to the west by an area characterised by NW verging slides such as the Portsoy Slide (Coward, 1983a) and by further slides in the Dufftown and Glen Avon areas (J. Treagus, pers. comm.). This style of deformation is analagous to that a little to the southwest in the Central Highlands where similar NW verging slides occur in the Braemar area (P. Brown & J. Treagus, pers. comm.) and also further to the southwest (Bradbury et al., 1979; Roberts and Treagus, 1979) (see figure 10.5). If the Banff Nappe is not allochthonous on the lower parts of the Dalradian stratigraphy, these slides must become vertical at depth. If they shallow out at depth, then they must underlie the Banff Nappe which would therefore be allochthonous. It is assumed reasonable by comparison with models for other orogenic belts, that these slides do flatten with depth. The present steep attitude of high strain zones, such as that at Portsoy, does not necessarily mean that original movement on them was subvertical. There are many mechanisms by which subhorizontal structural elements may be steepened where they lie in the interior portions of orogenic belts. Indeed, such steepening might be expected (Coward, 1983b).

It is not envisaged that only vertical movements occurred between the Buchan area and more S (Tay Nappe inversion) and W (areas to the west of the Portsoy Slide) areas. If the shear zones do represent zones on which original movement was vertical, this does not preclude earlier structural relationships of a different character.

In the following discussions, the Banff Nappe is defined as comprising units above the Portsoy Thrust. It is envisaged as overlying the core of the Tay Nappe to the SE and the lower parts of the Dalradian stratigraphy to the northwest, and as stratigraphically correlatable with

the Southern Highland and upper Argyll Group Dalradian of the Central Highlands (figures 10.5 and 10.6). A simple model for the structural evolution will be followed. SE directed deformation resulted in the formation of the Tay Nappe, during which the Banff Nappe was thrust southward to overlie the core of the Tay Nappe. This regime was followed by one in which parts of the Tay and Banff areas were thrust to the NW over the lower parts of the Dalradian stratigraphy.

10.4 DIFFERENTIAL UPLIFT

The array of recorded pressures preserved within the Dalradian (figure 10.7) indicates that considerable differential uplift has occurred. Different areas must have followed considerably different P-T-t paths. Minimum pressure conditions occur in the centre of the Boyndie Syncline in the Buchan area. Pressures are probably about 2- 3kb (see Hudson,1980). This compares with about 10kb in the Central and SW Highlands and about 7-8kb in Glen Muick and the Duchray Hill Gneiss. It appears that rocks in the Boyndie Syncline have never been buried to depths much greater than recorded by their present mineral assemblages. Rocks in the Central Highlands might potentially have experienced eclogite facies conditions. The crust was at least doubled in thickness in this area, more if significant preorogenic basin extension occurred.

The relative exhumation of more S, W and SW areas must be explained tectonically. Harte and Hudson (1979) proposed that it occurred primarily as the result of post metamorphic folding. Other possibilities could be suggested. Rotation of parts of the crust might occur through some other process apart from the formation of simple anticlines and synclines. Movement on a series of steep faults could be invoked. This appears unlikely as the recorded array of pressures is apparently not discontinuous against any major faults. Alternatively such rotation might

be caused as the result of structurally lower and later sliding or as the result of isostatic bending of the crust (see Coward,1983b).

10.5 RELATIONSHIPS OF METAMORPHISM TO STRUCTURE

In E Scotland, lower P/T rocks (Buchan facies series D and E) occur within the Banff Nappe while Barrovian facies series (B) occurs within the Tay and Tarfside (Harte,1979) Nappes. The sillimanite zone is restricted to the Banff and Tay Nappes. In the Tay Nappe to the west the metamorphism is of a higher pressure Barrovian type, but the sillimanite zone is not reached at the higher grades. To the NW of the Banff Nappe, the andalusite zone grades into the higher pressure kyanite zone. Higher structural levels (i.e. the Buchan area comprising the Banff Nappe) are suggested to have been metamorphosed as a result of additional heat input and have flatter heating paths. Lower structural levels in the south (i.e. the Tay Nappe inversion) were probably subject to a combination of tectonic thickening and heat input. Areas to the west and southwest of the Banff area perhaps experienced only tectonic thickening (see chapters 7 & 8).

Examination of figure 10.7 shows that rocks at the higher structural levels were generally metamorphosed at higher temperatures than those at lower structural levels to the west and to the south. Similarly the Tay Nappe was metamorphosed at lower temperatures than areas structurally above in the sillimanite zone. Temperatures increase from low structural levels in the NW to the sillimanite zone at high structural levels in the SE.

It has been suggested that the Newer Gabbros were the cause of the sillimanite overprint and of generally higher temperatures in NE Scotland. In support of this contention might be cited the apparent close association of sillimanite zone metamorphism with some of the gabbros. Newer Gabbro associated metamorphism overprints regional metamorphic zones around Portsoy (Ashworth,1975). Against this assertion, it can be

observed that hornfelsic rocks are usually very localised near the margins of the intrusions. Away from the gabbros, high grade rocks carry strong regional fabrics (e.g. in the Cowhythe Gneiss) suggesting that they may not be the result of contact metamorphism. Fettes (1970) has demonstrated the very localised effects of the Newer Gabbros. Contact metamorphic zones around the Inch gabbro are very narrow. Some high grade rocks in Cromar/Glen Muick and the Duchray Hill Gneiss are unrelated to any Newer Gabbro and must be "regional" in origin. In summary, relatively high temperature metamorphic rocks at high structural levels are at most only partially attributable to Newer Gabbro intrusion. Other deep level heat sources may of course have been operative.

One can propose two contrasting models to explain the presence of high temperature rocks at high structural levels:

(a) Metamorphism occurred after all important structural events apart from gentle post metamorphic folding. Differences in temperature between the Buchan area and the Central Highlands are related to lateral differences resulting from an extraneous heat source superimposed on an already restacked crust at a late stage. Pressure variations are related to simple post metamorphic folding. This model is apparently that envisaged by Harte and Hudson (1979) (figure 10.8).

(b) Synmetamorphic thrusting occurred. Differences in temperature reflect original vertical differences now variably preserved due to later deformation, thrusting and back rotation. Rocks now beneath the Buchan area would have been cold originally and would have heated up after overthrusting of structurally higher units. The extraneous heat source was imposed upon Buchan rocks before rather than after crustal restacking. Pressure differences are related to a number of factors which influence the P-T-t paths of rocks (see figure 10.9).

The distinction between these two hypotheses rests upon evidence for the relative timing of thermal and deformational events in different areas. Conventional structural correlations in the Dalradian suggest that the high temperature sillimanite zone metamorphism is a late feature regionally rather than just late locally. It seems that the timing of sillimanite growth with respect to phases of deformation outside the sillimanite zone is an open question. The structural correlations involved are often based just on relative chronology (e.g. Harte and Hudson, 1979).

It can be observed that porphyroblast growth in the areas to the west of the Banff Nappe and to the north of the flat belt of the Tay Nappe was often syntectonic and occurred during NW sliding (see table 1.2). At Portsoy, the transformation of andalusite to kyanite, with an implied pressure increase, occurred during sliding (Treagus and Roberts, 1981). These observations indicate that porphyroblast growth in these parts of the Dalradian was broadly syntectonic and that restacking of the crust accompanied peak metamorphism. This supports the second model.

The western boundary of the Banff Nappe at Portsoy is marked by a steep zone. This comprises a zone of intense deformation, the Portsoy Slide Zone, which may be related to northwesterly directed movement (Treagus and Roberts, 1981; Coward, 1983a). The stratigraphy, the lineation related to the Portsoy Slide Zone and the late shear zone are all orientated steeply. The stratigraphy youngs to the east through Portsoy. At some stage either after or before the metamorphic climax the stratigraphy was rotated from a subhorizontal to a subvertical position. If rotation was post metamorphic, then the heat source must have been imposed on Buchan rocks before crustal restacking because the rocks that would have been beneath the Buchan area after overthrusting (eg. the Dalradian rocks to the west of Portsoy) show no signs of the imposition of

the heat source. There are reasons for believing that this rotation occurred after metamorphism rather than before. These are:

(1) Johnson (1962) noted that there are many monoclinial steps on the western limb of the Boyndie Syncline. These steps (D3 folds) deform an earlier fabric related to the Boyndie Syncline. They may have been responsible for the rotation of stratigraphy, metamorphic zones and D2 lineations into a subvertical position (see Johnson,1962).

(2) The distribution of rocks that achieved different metamorphic pressures implies rotational movements after metamorphism. Pressures increase from the centre of the Boyndie Syncline to Portsoy and to the west of the Buchan area (figure 10.7). The preserved facies series along this transect is very steep (Hudson,1980). Assuming that they were recorded synchronously these pressures imply post metamorphic rotation of up to about 45° if the rotation was distributed evenly. If the rotation was concentrated in particular zones, steep belts could be produced. A number of flat and steep belts are found along the north Buchan coast.

(3) If a heat source was imposed on Buchan rocks after their restacking, it would be expected that the sillimanite zone would crosscut stratigraphy to a greater extent than it does. In fact the sillimanite zone is restricted to the proposed Banff Nappe in this part of the Dalradian. It is also noticeable that the Newer Gabbro suite are entirely restricted to the Banff Nappe.

(4) Cumulate layering in the Huntly-Portsoy Newer Gabbro is steeply orientated (Munro,1970). The Newer Gabbros are thought to slightly postdate the peak of Buchan Metamorphism (Pankhurst,1970) implying that rotation occurred after metamorphism. However, it is possible that the steep attitude of the layering might be attributable to late shear zones described by Ashcroft et al. (1984).

Droop and Charnley (1984) have estimated pressures of metamorphism in the aureoles of the Newer Gabbro intrusions. These are about 4.5kb for all the gabbros studied, implying that no net tilting has occurred in NE Scotland since their intrusion at about 490Ma (Droop and Charnley,1984). If the Newer Gabbros were all intruded at a given depth, then folded and then the area tilted all Newer Gabbros exposed would then record the same pressure. If there has been no tilting of NE Scotland at all since the time of Newer Gabbro intrusion this would be difficult to reconcile with the rotation of metamorphic zones after Newer Gabbro intrusion. No rotation of the Newer Gabbros has occurred since they cooled through about 550°C at about 470Ma (Sallomy and Piper,1973).

If extensive vertical movement occurred on the shear zone to the west of the Morven Cabrach and Huntly Portsoy Newer Gabbros it would be expected that a considerable pressure differential would exist across this zone. Although there appears to be a rapid transition to lower temperatures pressures are comparable. To the east 4.5kb is recorded from the aureoles of the two Newer Gabbros (Droop and Charnley,1984) while to the west pressures of about 4kb are indicated by the coexistence of andalusite, kyanite with rare fibrolitic sillimanite at Portsoy. This suggests that most of the relative movement between these areas was horizontal rather than vertical.

It appears that the pressure increase to the west of the Buchan area is, at least on a large scale, continuous. If areas to the west were thickened by exotic nappes which did not cover the Banff area, and later differential uplift occurred along the steep shear zones, then continuity in recorded pressures would not be expected between Banff and more westerly areas. The greater, but gradually increasing metamorphic

pressures to the west are most easily explained if the Banff Nappe, itself, provided the thickening.

10.6 THE PORTSOY ZONE

The Portsoy Zone (figure 10.10) comprises a complex zone at the base of the Banff Nappe. To the east lies the Cowhythe Gneiss which reaches sillimanite-K-feldspar grade. Further eastwards, towards higher structural levels, the pressures and temperature decrease towards the biotite zone in the centre of the Boyndie Syncline (Hudson,1980). The Cowhythe Gneiss abuts a complex zone in which the deformation is intense.

To the west of the Cowhythe Gneiss, the grade decreases suddenly to andalusite kyanite schists, and thereafter temperatures decrease to the west (see chapter 7). A temperature maximum is reached in the Cowhythe Gneiss.

The structure of this coastal section has recently been treated by Treagus and Roberts (1981). Their local D2 deformation is most intense in the region of Portsoy. It dies out structurally downwards to the west and does not extend above the top of the Cowhythe Gneiss to the east. The deformation is characterised by steeply dipping fold axes and mineral lineations. The intensity of deformation in the Portsoy Zone suggests that a slide is present. The steeply dipping lineation may give the direction of movement. Folds have been tightened and rotated into the extension direction (Coward,1983a; Treagus and Roberts,1981). The dip of fold axes suggests NW directed movement in agreement with other lineations in Dalradian slide zones (Coward,1983a; Shackelton and Ries,1984). This deformation may relate to the emplacement of the Banff Nappe. Local D3 is limited to the steep limb of the Boyndie Syncline according to Treagus and Roberts (1981) (figure 10.11), and may be responsible for steepening the dip of rocks in the Portsoy Zone. It has also been suggested (Ashcroft et al.,in press) that the Portsoy Zone contains a late shear zone. To the

west of the sillimanite gneisses, a tectonic mixture of different lithologies occurs in a matrix of pelitic schist (Sutton and Watson, 1956). Blocks of quartzite, limestone, serpentinite, gabbro and anorthosite occur.

Porphyroblast growth in the Buchan zones to the east of Portsoy occurred during a static hornfelsing episode between the local D1 and D3 deformations (Hudson, 1980; Treagus and Roberts, 1981). To the west of Portsoy, porphyroblast growth occurred during local D2, except for andalusite which appears to predate these movements (Johnson, 1962; Treagus and Roberts, 1981). Andalusite was replaced by kyanite during D2. This replacement may reflect increasing pressures as a result of a D2 emplacement of the Banff Nappe.

Portsoy Gabbro

It is uncertain to what extent the high grade metamorphism in the Cowhythe Gneiss is related to the various masses which compose the Huntly Portsoy Newer Gabbro. Ashworth (1975) mapped mineral zones in the area around the gabbro and concluded that they were related to its intrusion. He suggested that the sillimanite zone is Newer Gabbro related and overprints an earlier direct transition from regional kyanite to andalusite zones. Hornfelses are only locally present around the margin of the gabbro. At any distance away from the contact there is a strong biotite fabric with no development of hornfelsic biotites across the schistosity. Two conclusions seem possible; that the Newer Gabbro was not responsible for metamorphism away from its vicinity, or that the Newer Gabbro was intruded during an active period of deformation.

The Portsoy Gabbro is of debatable local structural age. It has in the past been considered of "older" (pre-deformational) origin (Read, 1923). Its intensity of deformation varies considerably from intensely lineated in the west to apparently little deformed in the east.

Stewart and Johnson (1960) suggested that two gabbros were present, a westerly intensely lineated Older Gabbro and an easterly essentially unlineated Newer Gabbro, supposedly separated by a very thin belt of contact metamorphosed metasediment. Examination of the easterly gabbro, however, shows that it does at least locally carry a steeply plunging lineation, presumably the equivalent of that in the Portsoy Group to the immediate west, though not nearly so intense. Photomicrographs of lineated gabbro are shown in figures 10.12 and 10.13. There is a gradual increase in the intensity of deformation of the gabbro from east to west. It is concluded in agreement with Read (1923) that the gabbro is one, variably deformed body, not two separate bodies. Any difference in the degree of deformation may be attributed to heterogeneity of deformation.

If the gabbro is "Newer" then its aureole is strongly attenuated to the west (see figure 10.14). This might be explained by deformation causing tectonic attenuation of the western part of the aureole, either as the result of movement within the slide zone or as the result of later shear zone movement. It is striking that no contact metamorphic aureole is discernable to the west of the Portsoy Gabbro. To the east of the gabbro, cordierite-K feldspar gneisses occur (Ashworth, 1975). Calcareous schists attributed to the Portsoy Group are found between the gabbro and the base of the Cowhythe Gneiss. They contain the assemblage biotite-plagioclase-quartz-tremolite-garnet. Garnet-biotite temperatures are about 550°C for this band, but the garnets are very manganese rich. Considering the poorly constrained thermodynamic mixing properties of spessartine garnets, caution should obviously be exercised. If the temperatures are realistic, then they must indicate tectonic intercalation of relatively low grade rocks between Cowhythe Gneiss and Portsoy Gabbro.

Alternatively, one might view the effects of the Newer Gabbros as very localised and the Cowhythe Gneiss as regional in origin. If so, there is still a very rapid transition between sillimanite-K feldspar gneisses and andalusite-kyanite schists which requires explanation.

10.7 DIACHRONEITY?

It has been suggested that Buchan metamorphism and more westerly kyanite zone metamorphism were contemporaneous (Johnson,1962). There seem few grounds for such an assertion. There is some evidence of a controversial nature from within the Portsoy Zone which may suggest diachroneity of Buchan and western kyanite zone metamorphism.

The suggestion that the Portsoy Gabbro is one body and is deformed by the local D2 (Treagus and Roberts,1981) in the west implies either :

(a) the Portsoy Gabbro is Older and is not responsible for migmatiation in the Cowhythe Gneiss. The Cowhythe Gneiss is regional in origin.

or

(b) the Portsoy Gabbro is Newer in origin and has been deformed by the local D2 lineation in the west. The Newer Gabbros predated NW movement of the Banff Nappe.

The first possibility requires that an explanation be found for the high grade rocks in the Cowhythe Gneiss which is found juxtaposed with lower grade andalusite-kyanite schists in the Portsoy Group. A tectonic explanation is appropriate. The second would be evidence of diachroneity. The Newer Gabbros slightly postdate the peak of Buchan metamorphism (Pankhurst,1970; Ashworth,1975) while porphyroblast growth to the west spanned D2 (Treagus and Roberts,1981). This might be indicative of diachroneity, but not necessarily so if D2 was a long lasting and diachronous deformational event.

It is claimed that steeply dipping folds correlated with D2, W of Portsoy postdate migmatiation within the Cowhythe Gneiss (Ramsay and

Sturt,1979). Ashworth (1979) adopts the structural chronology of Johnson (1962) and asserts that migmatisation was later than all the folding. Migmatitic leucosomes are certainly folded by the steeply dipping folds, but it is questionable whether melting occur before or after the various deformations. Ashworth (1979) contends that leucosomes carry no fabric either as the result of local D2 or D3.

Examination of fabrics in migmatitic leucosomes from the eastern side of Links Bay shows variable traces of deformation. In a band near the base of the nappe some are intensely deformed, as stated by Ramsay and Sturt (1979). Further to the east, some carry no obvious trace of deformation while others are variably deformed. It is possible to observe:

- (1) cracking of large feldspars and growth of alteration products along these cracks;
- (2) development of new quartzs and feldspars around the margins of large feldspar porphyroclasts;
- (3) change in grain shapes to become elongate within the foliation.

Deformed leucosomes sometimes pass into ones in which deformation is not obvious with random granoblastic textures. Some of the deformation is apparently associated with folds with steeply dipping axes (D2?).

Retrogressive muscovite is developed in the zone adjacent to the base of the Cowhythe Gneiss.

If the Newer Gabbros predate local D3 (Fettes,1970) and if monoclinial D3 folding did involve the rotation of various planar elements into the vertical, the Buchan rocks must have been metamorphosed before their emplacement on top of what are presently kyanite zone rocks or they too would have experienced the heat source. This would suggest that Buchan metamorphism predated D2 to the west of Portsoy.

At Portsoy, andalusite is replaced by kyanite during D2 (Treagus and Roberts,1981). Buchan andalusite is overprinted by a higher pressure

metamorphism suggesting that the kyanite zone metamorphism is later. The implied increase in pressure synchronous with D2 may reflect emplacement of the Banff Nappe.

10.8 SOUTHWARDS

The aureole of the Morvern Cabrach Newer Gabbro to the south of Portsoy is also attenuated to the west (Allan, 1970). Presumably this can be attributed to a process of tectonic attenuation similar to that which may apply in the case of the Huntly-Portsoy Newer Gabbro. Ashcroft et al. (1984) locate one of their shear zones along its western margin (figure 10.4) on the basis of the continuation of a metabasite train (see below).

Glen Muick

In Glen Muick and Glen Gironck, the sharp thermal break between high grade gneisses and lower grade kyanite-staurolite schists (chapter 3) might also be attributable to such a process. The zone in Glen Gironck with a steeply dipping mineral/fold axis lineation may be comparable to that at Portsoy. The Glen Doll Fault of Barrow and Cunningham Craig (1913) was considered to coincide with this mafic ultramafic band in Glen Muick. There is no other evidence for its presence in Glen Muick other than the igneous rocks. The fact that the metagabbros are lineated and penetratively deformed suggests that the structural break is of a relatively early broadly synmetamorphic age. There is also a sharp thermal transition along the western margin of the Duchray Hill Gneiss. These breaks or sharp transitions in grade are attributed to a tectonic origin. A slide or series of slides are suggested to have been present along which high temperature rocks in the east and south Highlands were thrust to the NW.

10.9 METABASITES

The thermal discontinuities south of Portsoy coincide with a train of metabasites. Garson and Plant (1973) have suggested that this train is

continuous throughout the Dalradian. It consists of metagabbros, amphibolites, serpentinites and pillow lavas in various states of deformation. In NE Scotland, this linear array continues from Portsoy, southwards along the western margin of the Huntly Portsoy and Morven Cabrach Newer Gabbros, coincides with the thermal break in Glen Muick, and then passes to the west of high temperature rocks in the Duchray Hill Gneiss. Serpentinites in the Dalradian are apparently restricted to the Crinan Subgroup of the Argyll Group. More have recently been discovered from this horizon (Henderson and Robertson, 1982). In the southwest Dalradian the Tayvallich Lavas (basaltic) occur at a slightly higher stratigraphic level (Harris and Pitcher, 1975).

In NE Scotland, the age of such metabasites is the subject of debate. Two suites of basic rocks have been recognised in the past. The Older Gabbros are deformed, have sheared margins and lack contact metamorphic hornfelses. The later suite of Newer Gabbros was originally identified by their undeformed state and the presence of associated contact metamorphism. However, it has been recognised that many of the Newer Gabbros are extensively sheared by a set of regional amphibolite facies shear zones (Ashcroft and Munro, 1978; Ashcroft et al., 1984). In addition many of the bodies lack hornfelses on account of extensive post hornfelsing shearing of their margins.

The state of deformation of these bodies may not be the best means of separating them, given the possible heterogeneity and diachroneity of deformation. It would seem most appropriate to separate the two different suites on chemical criteria. For instance in Connemara striped amphibolites (probably analogous to the Older Gabbros) are separated from the Connemara Gabbros (which may be similar to the Newer Gabbros of NE Scotland) by the different chemical trends of the two suites (Yardley and Senior, 1982).

The train of metabasites leading southwards from Portsoy (figure 10.15) was originally recognised as Older in nature owing to their deformed nature, conformity with regional structural trends and lack of any trace of contact metamorphism. Rocks from this train may carry strong fabrics associated with regional deformation. The Portsoy Gabbro is intensely lineated and the gabbro between Glen Muick and Glen Girnock (chapter 3) also carries a strong fabric. In contrast, the leucogabbro at the NW margin of the Morven-Cabrach intrusion (A in figure 10.15) is little deformed and carries much igneous clinopyroxene. None of these bodies have detectable associated contact metamorphic hornfelses. It has recently been proposed that some of the train belong to the Newer suite (D. Fettes, pers. comm.) on account of lack of deformation of some bodies. It seems likely that the intensely deformed bodies, at least, were emplaced at an early stage in the local structural history. Chemical data are required in order to attempt to differentiate the two suites.

The linear array of metabasites requires explanation. Alpine type mafics and ultramafics may represent disrupted ophiolitic material, basal arc intrusions or diapirically or tectonically emplaced intrusions (Misra and Keller, 1978). The possibilities for the genesis of these bodies, given that they lie in a linear array may be summarised as follows:

(a) The intrusions are structurally controlled. Shear zones in the eastern parts of the Buchan area are characterised by arrays of variably deformed metabasites (Kneller and Leslie, 1984). The metabasite array under consideration may relate to some such shear zone or to some other structural lineament.

(b) The metabasites may date from very early in the evolutionary history of the Dalradian Basin. Graham and Bradbury (1981) describe metabasites from further west which include lavas and intrusions and which they relate, on account of their chemistry, to an early basin spreading event.

Some of the metabasites in NE Scotland may have had a similar origin. If so their arrangement in a linear array must be explained. If the metabasites were intruded into a preexisting sedimentary pile, it seems hard to explain their close correspondence to a given stratigraphic level. They may have been intruded along the locus of maximum stretching. This axis may have become the site of a later tectonic boundary.

(c) A rather more extreme suggestion is that the NE Scotland train of metabasites represents a dismembered ophiolite (Garson and Plant,1973; Dewey,1982). It is not generally thought that oceanic crust existed within the Dalradian basin (Harris et al.,1978). However, there are some contrary suggestions (Kennedy,1980). It is certainly not impossible that oceanic crust existed within parts of the Dalradian basin, considering the large amounts of stretching that may have been involved (see Dewey,1982). The association of ultramafics, amphibolites, metagabbros and occasionally pillow lavas (MacGregor and Roberts,1963) would be appropriate for a disrupted ophiolite. Some of the metabasite associations are similar to those of unequivocal deformed ophiolites (e.g. Misra and Keller,1978; Drake and Morgan,1981; Boudette,1983; Kite and Stoddard,1984). In SW Scotland, these metabasites are not associated with any known structural break although they are of spreading centre type (Graham and Bradbury,1981). In SW Scotland metabasites consist of many dykes and sills which could not relate to an ophiolite stratigraphy. It should be emphasised that no ophiolite stratigraphy is recognised in the Scottish or Irish Dalradian, although it has been suggested that rocks within the Highland Border Complex at the southern limit of the Dalradian are ophiolitic and originate from within the Dalradian basin (Henderson and Robertson,1982; Ryan et al.,1983). There is a zone of syngenetic pyrite-chalcopyrite mineralisation associated with a similar stratigraphic

horizon to the metabasites similar to that found in many ophiolites (Smith,1977).

(d) A particular level of the crust, characterised by a suite of such intrusions, might have been exhumed tectonically. Metabasites might, for instance, have been intruded at the lower levels of a stretched Buchan crust. Later rotation and exhumation of these rocks might produce a linear array of metabasites.

These possibilities are consistent with various models for the evolution of the area. It does, however, seem that the array of metabasites must confirm the presence of some structural break or lineament. Garson and Plant (1973) have suggested the continuity of this array of alpine type ultramafics throughout the Dalradian and have advocated the presence of a major structural break. In the SW Highlands the lavas and intrusions occur at a slightly higher stratigraphic level and there is apparently no evidence for the presence of any structural break. It is possible that different parts of the Dalradian may have been characterised by different amounts of preorogenic spreading. Some may have been ensialic with extensive dyke and sill intrusion (SW Highlands), some may have resulted in local production of oceanic crust (perhaps in NE Scotland?). If spreading was more marked in the NE, this might result in a more obvious structural boundary in that area. If a structural break does coincide with the linear array of metabasites, no other evidence for it is available in the SW and Central Highlands. It is possible that the evidence for an early structural break might be unrecognised if it was associated with discrete thrusting and non-penetrative deformation.

10.10 SUMMARY

The Banff Nappe is believed to be allochthonous on more westerly rocks on account of:

- (1) evidence for post metamorphic steepening of structural elements;
- (2) apparent continuity in recorded metamorphic pressures across the margin of the Banff Nappe;
- (3) preferred models for the structural evolution of such belts (e.g. Coward, 1983b).

The following features are found to be associated with the base of the Banff Nappe:

- (1) A temperature maximum is reached to the immediate east. The sillimanite zone and migmatisation do not extend to the west. Temperatures decrease gradually to the west to the lowermost Dalradian.
- (2) Thermal features are sharp adjacent to the base of the nappe. Rapid transitions occur to lower grade. Aureoles of synmetamorphic intrusions are attenuated, though this may be due in part to later shear zones.
- (3) A zone of intense deformation is found at Portsoy, characterised by a lineation plunging steeply towards the SE. This may be associated with NW thrusting. A similar zone lies to the west of Glen Muick. Late shear zones may also be located along this margin.
- (4) A train of metabasites occurs of uncertain significance. It seems likely that the linear array documents the presence of some structural break.

These observations suggest that the Portsoy Zone marks an important structural break.

10.11 GEOCHRONOLOGICAL EVIDENCE

A chronology of events in NE Scotland, based on data in the literature, is presented in table 10.1. Of particular interest is the relative chronology of peak metamorphism and later cooling. Unfortunately, constraints are not as good as might be wished. There are tentative indications that:

(1) metamorphism was earlier in the sillimanite zone than near the Highland Boundary Fault;

(2) metamorphism was earlier in the Dalradian than in the Moine to the north of the Great Glen Fault.

Anatectic crustally derived granites might provide some indications of the relative ages of thermal events. These occur at 514 to 480Ma (Central Highlands), 470 to 440Ma (Banff-Buchan area) and around 445Ma in the southern Moines. There is a suggestion of SE to NW diachroneity of thermal events from the data (see references in chapter 1).

K-Ar and Rb-Sr cooling ages are presented in figure 10.16 from Dewey and Pankhurst (1970) and Dempster (1984). In the Glen Esk area rapid uplift occurred at 460Ma, while in the sillimanite zone to the north temperatures fell below the Rb-Sr muscovite closure temperature by 515Ma (Dempster, 1984). K-Ar mica ages of about 460Ma in the Buchan area are generally earlier than those in the Moine to the northwest.

This evidence is broadly in agreement with the model presented above. Metamorphism was earlier in the sillimanite zone, later in the Tay Nappe to the south, and perhaps later to the northwest. Cooling occurred earlier in the southeasterly areas (i.e. Tay and Banff Nappes) than further to the northwest.

10.12 SYNTHESIS

A model for Dalradian thermal evolution is proposed on the basis of some simple assumptions about the structural evolution; that the Buchan area is allochthonous with respect to more SE and NW areas, and that SE verging Tay Nappe formation was superseded by much NW verging deformation. The following chronology of events is envisaged.

(1) Deposition of the lower to middle Dalradian occurred on the continental shelf. The "upper" Dalradian (Crinan subgroup of Middle Dalradian and above) area of deposition may have been further removed from

the continental margin. Basin stretching during this period resulted in multiple dyke intrusion and tholeiitic volcanism. Oceanic crust may have been produced in some areas (figure 10.9a A).

(2) Early thrusting and sliding, which commenced before 515Ma, was SE directed. At some stage during this SE directed thrusting an external heat source was imposed on what is now the Buchan area. This led to the development of cordierite through andalusite through sillimanite facies series. This high temperature metamorphism may have been the result of metamorphism in an arc environment or in an extended Buchan crust (figure 10.9a B & C).

(3) During continued SE directed sliding hot rocks at the base of the Banff Nappe (i.e. sillimanite zone in Glen Muick) slid southwards to overlie the lower limb of the Tay Nappe. This SE directed sliding may have resulted in an inverted gradient within the Tay and Tarfside Nappes. The inverted isograds, if they exist, must be related to underthrusting, below the present level of exposure, and to overthrusting of hot Buchan rocks. Inverted isograds which may have existed after overthrusting are now partially preserved, owing to continued tectonic convergence, followed by rotation of the crust from the horizontal towards the vertical. Thus metamorphic temperatures commonly decrease towards lower structural levels (figure 10.9a D).

Metamorphism in Barrows zones may be contrasted with that in the Central Highlands (figure 10.9b A). Lower temperatures at greater depths may have been achieved owing to greater distance from the Buchan heat source.

(4) Newer Gabbro intrusion occurred at about 490Ma. This intrusion is likely to have occurred while NW directed sliding was occurring.

(5) NW directed sliding was operative by 510Ma (date of the Ben Vuirich Granite). This resulted in the tectonic burial of rocks to the west of the

Banff Nappe (west of Portsoy) and to the north of the Tay Nappe flat belt (figure 10.9a-E & 10.9a-B).

(6) Thermal relaxation resulted in increasing temperatures in tectonically buried rocks, leading eventually to the growth of kyanite.

(7) Later isostatic bending of the crust or sliding at deeper structural levels, concomitant with folding at the higher structural levels and resultant erosion resulted in the exhumation of tectonically buried rocks. The status of the shear zones in such a model is uncertain. They may reflect a late zone of differential vertical movement between higher and lower structural levels. However vertical movement on them cannot be enormous owing to the apparent continuity in pressure across them.

(8) Late isostatic uplift occurred so that the presently exposed surface lay at a depth of about 6km by 400Ma.

Alternative Models

Alternative models will now be considered. Firstly, consider the initial situation in which the Buchan area directly overlaid rocks, presently to the west of Portsoy. This is essentially the model proposed by Harte and Hudson (1979). The following sequence of events may have occurred:

(1) Buchan area overlies area to the west of Portsoy either along a thrust or as the result of original stratigraphic relationships.

(2) Metamorphism develops characterised by a depth controlled transition from andalusite to kyanite zones (figure 10.8).

(3) Extraneous heat input and locally the Newer Gabbros caused the development of sillimanite.

(4) later simple folding exhumed the lower rocks now exposed to the west of Portsoy. This is essentially the model proposed by Harte and Hudson (1979).

An extraneous heat source is thought to be responsible for the Buchan type metamorphism. The above hypothesis is tenable only if the heat source was very localised at high structural levels (e.g. the Newer Gabbros were responsible). Rocks originally below the Buchan area in the Harte and Hudson model and now exposed to the west of Portsoy show no evidence of this heat source. If additional heat was imposed on Buchan rocks before rotation, then the heat source must have been localised.

Another possibility is that the imposition of the heat source on the Buchan area occurred after folding. This possibility is not favoured because :

(1) the sillimanite zone records higher pressures than rocks in the centre of the Boyndie Syncline, but appears to record similar pressures to rocks west of Portsoy. This implies that metamorphism of rocks in the Buchan area occurred before some of the rotation.

(2) there is structural evidence of folding which postdated the intrusion of the Newer Gabbros which could have caused the required rotation.

Both classes of model, outlined above are considered unsatisfactory because:

(1) They do not take into account syntectonic porphyroblast growth to the west of Portsoy (Treagus and Roberts, 1981).

(2) They require the formation of many high amplitude anticlines and synclines which seem an unlikely structural style.

(3) The sillimanite zone and the Newer Gabbros are restricted to the Banff Nappe. (This is more easily explicable if this unit was far removed from units now to its west during metamorphism).

(4) They do not explain the decrease of temperatures to the west of the Portsoy Zone and its southerly extension.

In the models outlined above kyanite zone metamorphism to the west of the Banff Nappe would have predated sillimanite zone metamorphism.

Another model could be suggested in which the Banff area was never allochthonous on more NW areas to the west of Portsoy. A steep zone was formed at the margin of the Banff area at an early stage. In this instance, exotic nappes must be appealed to in order to provide the crustal thickening in areas outside the Buchan area. Sharp thermal transitions would be explained by late shear zones. This model is after Ashcroft et al. (1984).

This model is unsatisfactory because:

- (1) There is continuity in metamorphic pressures across shear zones at the western margin of the Banff area implying that differential vertical movement was small.
- (2) Structural models are preferred for the Dalradian in which crustal thickening was achieved by dominantly subhorizontal movements.
- (3) The present distribution of recorded pressure conditions implies that the Buchan area once overlay areas now to the west of Portsoy.
- (4) The model requires the presence of exotic nappes. It seems simplest to assume that structural units now at the highest structural level in the Dalradian provided this thickening.

These points are not compatible with an autochthonous Dalradian in NE Scotland. Neither of the models explains the coincidence of all the observed features with the base of the Banff Nappe.

10.13 THE GRAMPIAN OROGENY

Various models have been proposed to explain the evolution of the Grampian Orogeny. These comprise Andean type models (Phillips et al., 1976; Yardley et al., 1982) and collisional models (Lambert and McKerrow, 1976; Mitchell, 1984). Possible models will be commented upon in the light of the previous discussions. In so doing, only areas within the Moine and

Dalradian will be considered. Other tectonic blocks may have been juxtaposed at a relatively late stage and may have suffered an unrelated orogenic evolution (Yardley et al., 1982).

High pressures recorded in supracrustal rocks from the Scottish Highlands imply considerable crustal thickening. This thickening seems unlikely in anything other than a collisional event. The required pressures may be achieved within a plate margin subduction zone, but structural models for the Dalradian do not seem compatible with this idea. One must postulate the overthrusting of unit or units comprising a minimum of 30km at some stage during the Grampian Orogeny. The required overthrust thickness may or may not be provided by units preserved within the Dalradian.

An interesting feature of the Grampian Orogeny is the occurrence of high temperature low pressure metamorphic terrains within the upper parts of the Dalradian stratigraphy. The occurrence of Buchan/Glen Muick type metamorphism in NE Scotland has been the subject of discussion in earlier parts of this thesis. In the Irish Dalradian the sillimanite zones associated with metabasic intrusions in Connemara (Yardley, 1976; Yardley et al., 1979) and Tyrone (Cobbing et al., 1965) are comparable. High grade rocks in Connemara occur in the higher parts of the Dalradian stratigraphy which are correlatable with the NE Scotland Buchan rocks (Harris and Pitcher, 1975). They also occur at high structural levels with respect to northwest verging phases of deformation and structurally above lower grade rocks (see Tanner and Shackelton, 1979). Isograds may be inverted (see Badley, 1976). The Ox Mountains Granulites, which contain garnet-clinopyroxene metabasites and kyanite-K feldspar metapelites, are similar to the rocks described from Glen Muick. However they may have resulted from a Pre Caledonian event (see possibilities in Andrews et al., 1978).

Arc

There is evidence that an arc was developed along the southern margin of the Dalradian during the Grampian Orogeny. The trace element chemistry and mineralogy, calcic plagioclase, abundant magnetite and hornblende of the Connemara Gabbros suggests an origin in an arc (Yardley and Senior, 1982). Tremadocian basalts and andesites exist in S. Mayo to the north with similar arc affinities (Ryan et al., 1980). Yardley et al. (1982) suggest that similar rocks exist in the Curlew Mountains of N. Ireland. The basic intrusives of Tyrone and the Newer Gabbros of NE Scotland may, by analogy, be arc related. Those in Connemara are dated at 510 ± 10 Ma (Pidgeon, 1969) while those in NE Scotland date from ca. 490 Ma (Pankhurst, 1970).

The basic intrusives are all associated with high temperature metamorphism of low pressure type. This suggests that both are a common consequence of a particular thermal environment. These areas of synmetamorphic gabbros associated with sillimanite zone metamorphics all occur in the higher parts of the Dalradian stratigraphy. These high temperature rocks are also at high structural levels with respect to NW verging phases of deformation.

Discussion

The extension characterising the early phases of Dalradian history and evidenced by increasing basin instability and volcanic activity (references in chapter 1) was replaced later by a compressional phase. This must have occurred between the Middle Cambrian (see Harris and Pitcher, 1975) and 515 Ma, which is the end of the Cambrian according to the time scale of McKerrow et al. (1984).

In NE Scotland it is envisaged that an initial extensional regime progressively separated areas from the continental margin with the formation of a marginal basin. At a later stage an arc may have developed

in parts of the basin. This regime was superseded by a compressional one in which previously separated tectonic elements were collapsed back on to the continental margin. This change in environment from stretching to compression might result from a change in plate movement relative to a "fixed" subduction zone (Uyeda and Kanamori,1979).

The fact that high temperature metamorphics and synmetamorphic gabbros are associated with each other, always in the high parts of the Dalradian stratigraphy and at high structural levels may be significant. This association may represent the base of an arc (Yardley and Senior,1982). The heat source of the arc did not affect lower Dalradian shelf sediments as they were far removed at this time. The arc centres would have been localised, as other parts of the upper Dalradian stratigraphy appear to have been unaffected.

The orogeny may have occurred as the result of the collision of an arc system separated at an earlier stage from the continental margin. These terrains may never have been far removed from the continental margin.

10.14 CONCLUSIONS

A number of features are recognised as being coincident with the western margin of the Banff Nappe:

- (1) a maximum in metamorphic grade;
- (2) sharp thermal features;
- (3) a zone of intense deformation;
- (4) a train of metabasic rocks.

The Banff Nappe is considered to be an allochthonous body on both stratigraphically uppermost Dalradian to the south and stratigraphically lower Dalradian to the west. It is suggested that the Banff Nappe was first emplaced to the south and later to the northwest. Two phases of crustal thickening resulted from this emplacement. Later rotational

movements caused the exhumation of deeper structural levels. The general P-T-t paths and diachroneity of metamorphism may be explained in terms of this model. The thermal evolution of the Dalradian was profoundly influenced by the pattern of synmetamorphic deformation. The train of metabasites in the Dalradian is interpreted as having a tectonic significance.

The Grampian Orogeny is envisaged as consequent upon the collision of tectonic elements which were previously separated from the continental margin during marginal basin formation. Arc centres may have developed in some of these removed tectonic elements, leading to high temperature low pressure metamorphism.

CHAPTER 11

CONCLUSIONS

In this chapter a number of conclusions will be briefly reviewed. The discovery of high grade rocks in the Glen Muick-Cromar area suggests that the maximum regional conditions attained in the Dalradian were higher than previously envisaged. Furthermore it is implied that relatively low grade assemblages in these areas (andalusite and staurolite bearing assemblages) are not peak metamorphic. It has not been established whether all these assemblages relate to the intrusion of the Newer Granites at 400Ma or not. There are reasons for believing that some are not. It may be concluded that most staurolite and andalusite bearing assemblages in the southern part of the sillimanite zone are retrogressive (e.g. many of those detailed by Porteous (1973)). The status of muscovite in this respect might also be queried. Peak metamorphic muscovite may have been absent from much of the NE Scotland sillimanite zone. Two alternatives might have caused the development of these retrogressive assemblages:

- (1) fluid circulation during post peak metamorphic cooling perhaps involving fluid release during the solidification of partial melts.
- (2) extensive fluid circulation at about 400Ma due to the intrusion of the Newer Granites which are voluminous over much of the area.

There appears to be a sharp break in grade to the west of Glen Muick. Temperatures increase gradually from the chlorite zone near the Highland Boundary Fault to Glen Muick. To the west, temperatures decrease suddenly to kyanite-staurolite schists across a band of serpentinite and metagabbro. This sharp break in grade may be comparable with breaks in grade or rapid transitions to the west of the Cowhythe Gneiss and the Duchray Hill Gneiss. A tectonic hypothesis has been invoked.

A self consistent dataset has been derived for phases in the system KCMASHCO₂ using where necessary the MHSRK equation of Kerrick and Jacobs (1981). The resulting dataset contains heats of formation which are in good agreement with calorimetrically determined estimates. Using the

dataset a self consistent set of geobarometers has been derived. The calculation of some reactions involving ordered phlogopite using compositional data from natural assemblages does not give sensible answers. It is suggested that many natural biotites are disordered and that data for disordered phlogopite should hence be used.

Pressure and temperature estimation within the aluminosilicate zones has been attempted using a number of different methods including geobarometers based on the dataset. These mostly depend on the activity composition models for plagioclase and garnet. Alternative activity models from the literature would however affect pressure estimates by only a few hundred bars. The success of these attempts at estimation has been judged by the agreement of the estimates with the experimentally determined aluminosilicate phase diagram. Agreement appears to be very good. The use of this test might be criticised on the grounds of the common metastable persistence of aluminosilicate polymorphs during a prograde metamorphic event. The test would of course be invalid if the polymorphs persisted by several kbs and 100s of °C outside their stability fields during a prograde metamorphic event. It is possible that the coexistence of aluminosilicate polymorphs in the Dalradian may be, in part, a retrograde phenomenon.

Pressure temperature estimation coupled with calculation of the positions of dehydration reactions suggests quite low X_{H_2O} in many rocks, including the graphitic schists of the low kyanite zone. Systematic underestimation of temperature in the low kyanite zone compared to estimates from higher grade zones would permit higher estimates of X_{H_2O} .

The magnitude of pressure estimates is in many cases considerably dependent upon the temperature estimate. One particular problem is the estimation of garnet biotite temperatures at high grade with the

possible effect of various substitutions on biotite activity composition relationships and possibly significant retrograde reequilibration. For these reasons garnet biotite temperature estimates cannot be treated with too much confidence at the higher grades; garnet clinopyroxene and perhaps garnet amphibole exchange thermometry are to be preferred. There is some independent evidence for the higher grade temperature estimates presented (see below). In Glen Avon temperatures must lie below the equilibria marking the stability limits of the assemblages muscovite calcite-quartz, muscovite-zoisite-quartz, paragonite-quartz and calcite-rutile-quartz. Temperatures near the andalusite kyanite isograd, to the west of the sillimanite zone, must be below the aluminosilicate polymorph triple point. These constraints are satisfied in the low kyanite zone by the Ganguly and Saxena (1984) and the Hodges and Spear (1982) models of garnet biotite equilibria.

Temperature estimates in the Glen Muick area are particularly important to some of the authors' assertions. At the higher grades the following constraints are used to support the presented estimates:

- (1) appearance of clinopyroxene in metabasites (Spear, 1981).
- (2) melting reactions to produce tonalitic melts in metabasites (chapter 6).
- (3) the stability of staurolite+quartz.
- (4) agreement of garnet-clinopyroxene, -amphibole and -biotite exchange thermometers although the latter scatter somewhat.

A particularly important point to make is that different conclusions have been reached as a result of the assumptions used about the relative timing of metamorphism and deformation in orogenic belts. The authors' views may be summarised:

(1) the widespread correlation of deformation phases in the Dalradian has been carried out to far too great an extent. There seem little grounds for advocating D1, D2 etc. correlations covering large areas of the Dalradian. Structural correlations are only considered to be locally valid.

(2) It is thought that metamorphism is likely to be diachronous both for the reasons considered by England and Richardson (1977) and Wells (1979) (ie. different uplift rates and different initial crustal thicknesses) and because crustal thickening and heating are likely to have been diachronous from one part of the Dalradian to another.

It is suggested that there is no a priori reason for suggesting that any one aluminosilicate zone occurred before or after any other. Local sequences of polymorphs may have been established, but wider scale correlations are harder to justify. The high pressures and temperatures estimated for the Glen Muick area are obviously inconsistent with the simultaneous presence of an andalusite kyanite isograd in this area. The local sequence of polymorph development kyanite → sillimanite → andalusite indicates that the andalusite is post peak metamorphic. As a result of this observation two alternatives have been suggested:

(1) the andalusite kyanite isograd once lay to the north of Deeside.

(2) an andalusite kyanite isograd never existed within the sillimanite zone i.e. the sillimanite zone is primary. If an andalusite kyanite isograd ever existed within the sillimanite zone this isograd would have moved in space during evolving pressure temperature conditions ie. no one position of the isograd should be definable.

The regional survey of pressure temperature conditions suggests a preserved surface trajectory of decreasing or constant temperature and increasing pressure to the west of the andalusite kyanite isograd. In the Glen Muick area higher temperatures are estimated compared to "isogradic" syntheses, as the position of the andalusite kyanite isograd adopted in

these syntheses is not accepted. The thermochemical P-T synthesis presented in this work is preferred to the isogradic synthesis of previous authors owing to differences over position of the andalusite kyanite isograd and arguments about the diachroneity of peak metamorphic conditions and the relative timing of the aluminosilicate zones.

The high pressures estimated by Wells and Richardson (1979) are slightly reduced by the present estimates. This still implies a considerable pressure gradient between the andalusite kyanite isograd and Glens Avon and Ey, although of not so large a magnitude. This pressure gradient may reflect both a diachronous metamorphic imprint and considerable differential uplift. This differential uplift would have resulted in considerable rotation of the crust. Differential uplift is suggested to have occurred as a result of isostatic bending of the crust and deformation at deeper structural levels, causing back rotation and consequent erosion.

Clinopyroxene bearing amphibolites within the Moine originally contained a garnet-omphacite-quartz assemblage which has partially reacted to a hornblende plagioclase amphibolite. Unfortunately owing to the polyorogenic nature of the Moine it is not possible to constrain the age of these rocks. Garnet resorption textures occur in some Dalradian rocks. It is conceivable that these Dalradian rocks might have undergone similar reactions to the Moinian eclogites. Garnet resorption textures in Dalradian rocks probably reflect a decrease in pressure.

Other evidence for the pressure temperature evolution of the Dalradian is described in chapter 8. Evidence reported in the literature indicates that some pressure increase occurred during the metamorphic evolution. This is attributed to continuing crustal thickening during the metamorphism. Areas from the Central Highlands to Glen Clova underwent a

decrease in pressure during evolution through peak metamorphic conditions.

Evidence in support of this includes:

- (1) reactions involving the appearance of ilmenite and the disappearance of rutile.
- (2) garnet resorption in amphibolites.
- (3) retrograde zoning of plagioclase and adjacent garnet.
- (4) aluminosilicate polymorph relationships.

It is consequently suggested that sillimanite in the southern part of the sillimanite zone grew as a result of uplift, not as a result of an isobaric temperature rise. Uplift rates averaged for the first 100Ma after metamorphism are 0.1 to 0.2mm per year as indicated by pressures in contact metamorphic aureoles.

A model has been presented which attempts to integrate thermal and tectonic data from the Dalradian. This model has bearing on the status of a possible Banff Nappe. The first observation that has bearing on the structural status of the Buchan Zones is that there is structural, metamorphic and stratigraphic continuity between Tay Nappe flat belt and the Buchan area. This is not in accord with some suggestions that Pre Cambrian basement is present.

High temperature regional metamorphic rocks lie at high structural levels. The high temperature rocks are suggested to comprise an allochthonous unit, the Banff Nappe. It is suggested that emplacement of a Banff Nappe resulted in the deformation and metamorphism of structurally lower rocks. A number of features have been recognised as being coincident with the western margin of the Banff Nappe:

- (1) a temperature maximum is reached just to the east.
- (2) aureoles of synmetamorphic gabbros are attenuated against this line and a sharp break in grade occurs.

(3) a train of metabasites occurs.

(4) a zone of intense deformation occurs.

This model conflicts with a number of previous models, and prejudices some of which are summarised below:

(1) the present disposition of temperature and pressure is largely the result of a structural style involving the formation of anticlines and synclines of large amplitude (see Harte and Hudson, 1979).

(2) that the sillimanite zone is a late feature regionally. (It is not disputed that sillimanite is a late event in some areas, but it may not be late with respect to peak metamorphic conditions elsewhere).

(3) that Buchan and Barrovian metamorphism was contemporaneous.

(4) that the Buchan area is "autochthonous".

(5) that structural correlations covering very large areas of the Dalradian are valid.

In NE Scotland a linear array of metabasites occurs which is of relevance to models of early basin evolution. This linear array may represent:

(1) dismembered fragments of an ophiolite.

(2) metabasites intruded along some structural lineament.

(3) metabasites intruded preferentially at a given level in the crust and later exhumed as a result of tectonic rotation.

(4) represent the locus of maximum basin stretching during ensimatic basin evolution.

The deformation of some of the bodies implies that some are relatively early in the tectonic history.

Such considerations lead to a model for the evolution of the Dalradian during the Grampian Orogeny. During basin evolution crustal stretching resulted in tholeiitic volcanism and intrusion. At some stage

high temperature metamorphism occurred within parts of the basin; it is suggested as the result of the formation of an arc. Later movements are suggested to have caused the thrusting of these high temperature metamorphics across the continental margin and other parts of the Dalradian basin. This emplacement is suggested to have resulted in the deformation and metamorphism of structurally lower rocks. The closure of marginal basins locally containing oceanic crust might result in the formation of ophiolitic nappes with ages not much older than the age of emplacement (cf. Dewey and Shackelton, 1984).

REFERENCES

- AHRENS, T.J. & SCHUBERT, G. 1975. Gabbro eclogite reaction rate and its geological significance. *Rev. Geophys. Space Phys.* 13,383-400.
- ALLAN, W.C., 1970. The Morven Cabrach Basic Intrusion. *Scott. J. Geol.* 6,53-72.
- ALLEN, J.M. & FAWCETT, J.J., 1982. Zoisite-anorthite-calcite stability relations in H₂O-CO₂ fluids at 5000 bars: An experimental and SEM study. *J. Petrol.* 23,215-39.
- ANDERSON, P.A.M., & KLEPPA, O. J. 1969. The thermochemistry of the kyanite-sillimanite equilibrium. *Am. J. Sci.* 267,285-90.
- ANDERSON, P.A.M., NEWTON, R.C. & KLEPPA, O.J. 1977. The enthalpy change of the andalusite sillimanite reaction and the Al₂SiO₅ diagram. *Am. J. Sci.* 277,585-93.
- ANDERTON, R. 1982. Dalradian deposition and the late Precambrian-Cambrian history of the N Atlantic region: a review of the early evolution of the Iapetus Ocean. *J. geol. Soc. London* 139,423-34.
- ANDREASSON, P.G. & LAGERBLAD, B. 1980. Occurrence and significance of inverted metamorphic gradients in the western Scandinavian Caledonides. *J. geol. Soc. London* 137,219-30.
- ANDREWS, J.R., PHILLIPS, W.E.A. & MOLLOY, M.A. 1978. The metamorphic rocks of part of the south Central Ox Mountains of Counties Sligo and Mayo. *J. Earth Sci. R. Dubl. Soc.* 1,173-94.
- ANOVITZ, C.M. & ESSENE, E.J. 1982. Phase relations in the system CaCO₃-MgCO₃-FeCO₃. *EOS* 63,464.

- AN YIN, H. & GREENWOOD, H.J. 1983. Displacement of equilibria of OH tremolite and F tremolite solid solution. I Determination of the equilibrium P-T curve of OH tremolite. EOS 64,347.
- ASHCROFT, W.A., KNELLER, B.C., LESLIE, A.G. & MUNRO, I. 1984. Major shear zones and autochthonous Dalradian in the northeast Scottish Caledonides. Nature 310,760-62.
- ASHCROFT, W.A. & MUNRO, M. 1978. The structure of the eastern part of the Inch Mafic Intrusion. Scott. J. Geol. 14,55-80.
- ASHWORTH, J.R. 1975a. Staurolite at anomalously high grade. Contrib. Mineral. Petrol. 53,283-91.
- ASHWORTH, J.R. 1975b. The sillimanite zones of the Huntly Portsoy area in the northeast Dalradian, Scotland. Geol. Mag. 112,113-36.
- ASHWORTH, J.R. 1975c. Petrogenesis of migmatites in the Huntly Portsoy area, northeast Scotland. Min. Mag. 40,661-82.
- ASHWORTH, J.R. 1979a. Comparative petrography of deformed and undeformed migmatites from the Grampian Highlands of Scotland. Geol. Mag. 116,445-56.
- ASHWORTH, J.R. 1979b. Textural and mineralogical evolution of migmatites. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) The Caledonides of the British Isles-reviewed. Spec. Publ. geol. Soc. London 8,357-62.
- ASHWORTH, J.R. & CHINNER, G.A. 1978. Coexisting garnet and cordierite in migmatites from the Scottish Caledonides. Contrib. Mineral. Petrol. 65,379-94.
- ASHWORTH, J.R. & TYLER, I.M. 1983. The distribution of metamorphic temperatures around the Strontian Granodiorite. Geol. Mag. 120,281-90.
- ATHERTON, M.P. 1977. The metamorphism of the Dalradian rocks of Scotland. Scott. J. Geol. 13,331-70.
- ATHERTON, M.P. & SMITH, R.A. 1979. Chloritoid staurolite assemblages from Barrow's zones in Central Perthshire, Scotland. Geol. Mag. 116,469-76.

- ATTOH, K. & VAN DER MOLEN, J. 1984. Metamorphic temperatures in the Michigamme formation compared with the thermal effect of an intrusion, Northern Michigan. *J. Geol.* 92,417-32.
- BADLEY, M.E. 1976. Stratigraphy, structure and metamorphism of Dalradian rocks of the Maumturk Mountains, Connemara, Ireland. *J. geol. Soc. London* 132,509-20.
- BAILEY, E.B. 1928. Schist geology: Braemar, Glen Clunie and Glen Shee. *Trans. Roy. Soc. Edin.* 55,737-54.
- BAMFORD, D. 1979. Seismic constraints on the deep geology of the Caledonides of northern Britain. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.). *The Caledonides of the British Isles-reviewed. Spec. Publ. geol. Soc. London* 8,93-96.
- BARANY, R. 1962. Heats and free energies of formation of some hydrated and anhydrous sodium and calcium aluminium silicates. U.S. Bur. Mines Rept. Inv. 5900,17pp.
- BARANY, R. 1963. Heats of formation of gehlenite and talc. U. S. Bur. Min. Repr. Inv. 6251,9pp.
- BARANY, R. 1964. Heat and free energy of formation of muscovite. U. S. Bur. Repr. Inv. 6356, 6pp.
- BARNICOAT, A.C. 1983. Metamorphism of the Scourian Complex, NW Scotland. *J. metamorphic Geol.* 1,163-82.
- BARROW, G. 1893. On the intrusion of muscovite biotite gneiss in the southeastern Highlands of Scotland and its accompanying metamorphism. *Q. J. Geol. Soc. London* 49,330-58.
- BARROW, G. & CUNNINGHAM CRAIG, E.H. 1915. The geology of the districts of Braemar, Ballater and Glen Clova. *Mem. geol. Surv. U.K.*
- BECKER, H. 1972. Zur Bildung von Phlogopit in kieseligen Dolomiten. Unpubl. Diplom. Thesis, Tech. Univ. Hannover. (In Hoschek (1980)).

- BECKINSALE, R.D. & OBRADOVICH, J.D. 1973. Potassium argon ages for minerals from the Ross of Mull, Argyllshire, Scotland. *Scott. J. Geol.* 9,147-56.
- BELL, K. 1968. The age relations and provenance of the Dalradian series of Scotland. *Bull. geol. Soc. Am.* 79,1167-94.
- BELL, T.H. & RUBENACH, M.J. 1983. Sequential porphyroblast growth and crenulation cleavage development during progressive deformation. *Tectonophysics* 92,171-94.
- BEST, N.F. 1978. Mixed volatile equilibria in greenschist facies metabasalts. *Progress in experimental petrology*. N.E.R.C. Report 4,159-63.
- BIRD, G.W. & FAWCETT, J.J. 1973. Stability relations of Mg-Chlorite, muscovite and quartz between 5 and 10kb water pressure. *J. Petrol.* 14,415-28.
- BLENCOE, J.G. 1977. Molal volumes of synthetic paragonite-muscovite micas. *Am. Mineral.* 62,1200-15.
- BOETTCHER, A.L. 1970. The system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at high pressures and temperatures. *J. Petrol.* 11,337-79.
- BOHLEN, S.R. & ESSENE, E.J. 1977. Feldspar and oxide thermometry of granulites in the Adirondack Highlands. *Contrib. Mineral. Petrol.* 62,153-69.
- BOHLEN, S.R. & ESSENE, E.J. 1980. Evaluation of coexisting garnet-biotite, garnet-clinopyroxene and other Mg-Fe exchange thermometers in Adirondack granulites: Summary. *Bull. geol. Soc. Am.* 91,107-9.
- BOHLEN, S.R., PEACOR, D.R. & ESSENE, E.J. 1980. Crystal chemistry of a metamorphic biotite and its significance in water barometry. *Am. Mineral.* 65,55-62.
- BOHLEN S.R., WALL, V.J. & BOETTCHER, A.L. 1983a. Experimental investigation and geological applications of equilibria in the system

FeO-TiO₂-Al₂O₃-SiO₂-H₂O. *Am. Mineral.* 68,1049-59.

BOHLEN, S.R., WALL, V.J. & BOETTCHER, A.L. 1983b. Experimental investigation and application of garnet granulite equilibria. *Contrib. Mineral. Petrol.* 83,52-61.

BOUDETTE, E.L. 1982. Ophiolitic assemblage of early Palaeozoic age in the Central Western Appalachians. In St. JULIEN, P. & BELAND, J. (Eds.), *The major structural zones and faults of the northern Appalachians.* Geol. Assoc. Canada Spec. Paper 24,210-30.

BOUDIER, F. & NICOLAS, A. 1976. Interpretation nouvelle des relations entre tectonique et métamorphisme dans l'Ile de Groix (Bretagne). *Bull. geol. Soc. France* 18,135-44.

BRACE, W.F., SCHOLZ, C.H. & LAMORI, P. 1969. Isothermal compressibility of kyanite, andalusite and sillimanite from synthetic aggregates. *J. Geophys. Res.* 74,2089-98.

BRADBURY, H.J. 1979. Migmatization, deformation and porphyroblast growth in the Dalradian of Tayside, Scotland. In HARRIS, A.L. HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed.* Spec. Publ. geol. Soc. London 8,351-55.

BRADBURY, H.J. SMITH, R.A. & HARRIS, A.L. 1976. Older granites as time markers in Dalradian evolution. *J. geol. Soc. London* 132, 677-84.

BRADBURY, H.J., HARRIS, A.L. & SMITH, R.A. 1979. Geometry and emplacement of nappes in the Central Scottish Highlands. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.). *The Caledonides of the British Isles-reviewed.* Spec. Publ. geol. Soc. London 8,213-20.

BREWER, J.A. & OLIVER, J.E. 1980. Seismic reflection studies of deep crustal structure. *Ann. Rev. Earth Planet. Sci.* 8,205-30.

BREWER, J.A. & SMYTHE, D.K. 1984. MOIST and the continuity of crustal reflector geometry along the Caledonian-Appalachian orogen. *J. geol. Soc. London* 141,105-20.

- BREWER, M.S., BROOK, M. & POWELL, D. 1979. Dating the tectonometamorphic history of the southwestern Moine, Scotland. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. Spec. Publ. geol. Soc. London 8,129-38.
- BRIDEN, J.C., TURNELL, H.B. & WATTS, D.R. 1984. British palaeomagnetism, Iapetus Ocean and the Great Glen Fault. *Geology* 12,428-31.
- BROOK, M., POWELL, D. & BREWER, M.S. 1977. Grenville events in Moine rocks of the northern Highlands of Scotland. *J. geol. Soc. London* 133,489-96.
- BROWN, W.L. & PARSONS, P. 1981. Towards a more practical two feldspar thermometer. *Contrib. Mineral. Petrol.* 76,369-77.
- BROWN, G.C., CASSIDY, J., LOCKE, G.A., PLANT, J.A. & SIMPSON, J.R. 1981. Caledonian plutonism in Britain: a summary. *J. Geophys. Res.* 86,10502-514.
- BRYHNI, I. & BRASTAD, K. 1980. Caledonian regional metamorphism in Norway. *J. geol. Soc. London* 137,251-59.
- BURNHAM, C.W., HOLLOWAY, J.R. & DAVIS, N.F. 1969. Thermodynamic properties of water to 1000°C and 10,000 bars. *Spec. Paper geol. Soc. Am.* 132.
- BUTLER, R.H. 1982. A structural analysis of the Moine Thrust Zone Between Loch Eriboll and Foinaven, NW Scotland. *J. Struct. Geol.* 4,19-29.
- CARMICHAEL, D. 1969. On the mechanism of prograde metamorphic reactions in quartz bearing pelitic rocks. *Contrib. Mineral. Petrol.* 20,244-67.
- CHADWICK, B. 1968. Deformation and metamorphism in the Luckmanier region, central Switzerland. *Bull. geol. Soc. Am.* 79,1123-50.
- CHAPPELL, B.W. & WHITE, A.J.R. 1974. Two contrasting granite types. *Pacific Geology* 8,173-4.
- CHARLU, T.V., NEWTON, R.C. & KLEPPA, O.J. 1975. Enthalpy of formation at 970K of compounds in the system MgO-Al₂O₃-SiO₂ from high temperature solution calorimetry. *Geochim. Cosmochim. Acta* 39,1487-97.
- CHARLU, T.V., NEWTON, R.C. & KLEPPA, O.J. 1978. Enthalpy of formation of some lime silicates by high temperature solution calorimetry with

discussion of high pressure phase equilibria. *Geochim. Cosmochim. Acta* 42,367-75.

CHATTERJEE, N.D. 1976. Margarite stability and compatibility relations in CASH as a pressure temperature indicator. *Am. Mineral.* 61,699-709.

CHATTERJEE, N.D. & FROESE, E.F. 1975. A Thermodynamic study of the pseudobinary join muscovite-paragonite in the system $KAlSi_3O_8$ - $NaAlSi_3O_8$ - Al_2O_3 - SiO_2 - H_2O . *Am. Mineral.* 60,985-93.

CHATTERJEE, N.D. & JOHANNES, W. 1974. Thermal stability and standard thermodynamic properties of synthetic 2M Muscovite $KAl_2AlSi_3O_{10}(OH)_2$. *Contrib. Mineral. Petrol.* 48,89-114.

CHENEY, J.T. & GUIDOTTI, C.V. 1979. Muscovite plagioclase equilibria in sillimanite quartz bearing metapelites, Puzzle Mountain area, northwestern Maine. *Am. J. Sci.* 279,411-34.

CHERNOSKY, J.V. 1976. The stability of anthophyllite, A reevaluation based on new experimental data. *Am. Mineral.* 61,1145-55.

CHINNER, G.A. 1961. The origin of sillimanite in Glen Clova, Angus, Scotland. *J. Petrol.* 2,312-23.

CHINNER, G.A. 1962. Almandine in thermal aureoles. *J. Petrol.* 3,316-40.

CHINNER, G.A. 1966. The distribution of pressure and temperature during Dalradian metamorphism. *Q. J. geol. Soc. London* 122,159-86.

CHINNER, G.A. 1967. Chloritoid and the isochemical nature of Barrows Zones. *J. Petrol.* 8,268-82.

CHINNER, G.A. 1978. Metamorphic zones and fault displacement in the Scottish Highlands. *Geol. Mag.* 115,37-45.

CHINNER, G.A. 1980. Kyanite isograds of Grampian metamorphism. *J. geol. Soc. London* 137,35-39.

CHINNER, G.A. & HESELTINE, F.J. The grampide andalusite-kyanite isograd. *Scott. J. Geol.* 15,117-27.

- CIPRIANI, C., SASSI, F.P. & SCOLARI, A. 1971. Metamorphic white mica : definition of paragenetic fields. *Schweiz. Min. Petr. Mitt.* 51,259-302.
- CLARK, S.P. Jr. 1966. Handbook of physical constants. *Geol. Soc. Am, Mem.* 97. 587pp.
- CLAYBURN, J.A.P. 1981. Age and petrogenetic studies of some magmatic and metamorphic rocks in the Grampian Highlands. DPhil Thesis, Oxford (unpubl.).
- COBBING, E.J., MANNING, P.I. & GRIFFITH, A.E. 1965. Ordovician-Dalradian unconformity in Tyrone. *Nature* 206,1132-5.
- COWARD, M.P. 1983a The thrust and shear zones of the Moine Thrust and the NW Scottish Caledonides. *J. geol. Soc. London* 140,795-811.
- COWARD, M.P. 1983b. Thrust tectonics, thin skinned or thick skinned and the continuation of thrusts to deep in the crust. *J. Struct. Geol.* 5,113-24.
- CURRY, G.B., INGHAM, J.K., BLUCK, B.J. & ALWYN-WILLIAMS 1982. The significance of a reliable Ordovician age for some Highland Border rocks in Central Scotland. *J. geol. Soc. London* 139,453-456.
- CUTHBERT, S.J. HARVEY, M.A. & CARSWELL, D.A. 1983. A tectonic model for the metamorphic evolution of the basal gneiss complex , western south Norway. *J. metamorphic Geol.* 1,63-90.
- DAHL, P.S. 1980. The thermal compositional dependence of Fe^{2+} -Mg distribution between coexisting garnet and pyroxene application to geothermometry. *Am. Mineral.* 65,854-66.
- DAY, H.W. & KUMIN, H.J. 1980. Thermodynamic analysis of the aluminosilicate triple point. *Am. J. Sci.* 280,265-87.
- DEMPSTER, T.J. 1984. Localised uplift in the Scottish Dalradian. *Nature* 307,156-59.
- DEWEY, J.F. 1982. Plate tectonics and the evolution of the British Isles. *J. geol. Soc. London* 139,371-412.

- DEWEY, J.F. & PANKHURST, R.J. 1970. The evolution of the Scottish Caledonides in relation to their isotopic age pattern. *Trans. Roy. Soc. Edin.* 68,361-89.
- DEWEY, J.F. & SHACKELTON, R.M. 1984. A model for the evolution of the Grampian tract in the early Caledonides and Appalachians. *Nature* 312,115-21.
- DEWIT, M.J. & STRONG, D.F. 1975. Eclogite bearing amphibolites from the Appalachian mobile belt, NW Newfoundland. Dry versus wet metamorphism. *J. Geol.* 83,609-27.
- DRAKE, A.A. & MORGAN, B.A. 1981. The Piney Branch Complex-A metamorphosed fragment of the Central Appalachian Ophiolite in NW Virginia. *Am. J. Sci.* 281,484-508.
- DROOP, G.T.R. 1983. Pre alpine eclogites in the Pennine basement complex of the Eastern Alps. *J. metamorphic Geol.* 1,3-12.
- DROOP, G.T.R. 1983. Alpine metamorphism of pelitic schists in the southeast Tauern Window, Austria. *Schweiz. Min. Petr. Mitt.* 61,237-73.
- DROOP, G.T.R. & CHARNLEY, N.C. 1984. paper in press, *J. geol. Soc. London.*
- DROOP, G.T.R. & TRELOAR, P.J. 1981. Pressures of metamorphism in the thermal aureole of the Eive Granite Complex. *Scott. J. Geol.* 17,85-102.
- DYMEK, R.F. 1983. Titanium, aluminium and interlayer cation substitutions in biotite from high grade gneisses, west Greenland. *Am. Mineral.* 68,880-99.
- EGGERT, R.G. & KERRICK, D.M. 1981. Metamorphic equilibria in the siliceous dolomite system: 6kb experimental data and geological implications. *Geochim. Cosmochim. Acta* 45,1039-49.
- ELLIS, D.J. & GREEN, D.H. 1979. Effect of Ca on Fe-Mg Cpx-Gt exchange thermometry. *Contrib. Mineral. Petrol.* 71,13-22.

- ENGLAND, P.C. 1978. Some thermal considerations of alpine metamorphism. *Tectonophysics* 46, 21-40.
- ENGLAND, P.C. & RICHARDSON, S.W. 1977. The influence of erosion upon the mineral facies of rocks from different metamorphic environments. *J. geol. Soc. London* 134, 201-13.
- ENGLAND, P.C. & THOMPSON, A.B. paper in press, *J. Petrol.*
- ERNST, W.G. 1975. Systematics of large scale tectonics and age progressions: Alpine and circum Pacific blueschist belts successive underthrusting. *Tectonophysics* 26,229-46.
- ETHERIDGE, M.A., WALL, V.J. & VERNON, R.H. 1983. The role of the fluid phase during regional metamorphism and deformation. *J. metamorphic Geol.* 1,205-26.
- EUGSTER, H.P., ALBEE, A.L., BENCE, A.E., THOMPSON, J.B. & WALDBAUM, D.R. 1972. The two phase region and excess mixing properties of paragonite muscovite crystalline solutions. *J. Petrol.* 13,147-79.
- FAWCETT, J.J. & YODER, H.S. 1966. Phase relationships of chlorite in the system $MgO-Al_2O_3-SiO_2-H_2O$. *Am. Mineral.* 51,353-80.
- FERRY, J.M. 1981. Petrology of graphitic sulphide rich schists from south Central Maine: an example of desulfidisation during progressive regional metamorphism. *Am. Mineral.* 66,908-31.
- FERRY, J.M. & BURT, D.M. 1982. Characterisation of metamorphic fluid composition through mineral equilibria. *Reviews in Mineralogy*, vol 10. *Min. Soc. Am.* 207-62.
- FERRY, J.M. & SPEAR, F.S. 1978. Experimental calibration of the partition of Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.* 66,113-17.
- FETTES, D.J. 1970. The structural and metamorphic state of the Dalradian rocks and their bearing on the age of emplacement of the basic sheet. *Scott. J. Geol.* 6,103-7.

- FETTES, D. 1971. Relations of cleavage and metamorphism in the Macduff Slates. *Scott. J. Geol.* 7,248-53.
- FISHER, G.W. 1979. Rate laws in metamorphism. *Geochim. Cosmochim. Acta* 42,1039-50.
- FISHER, J.R. & ZEN, E. AN. 1971. Thermochemical calculations from hydrothermal phase equilibrium data and the free energy of H₂O. *Am. J. Sci.* 270,297-314.
- FLETCHER, C.J.N. & GREENWOOD, H. 1979. Metamorphism and structure of the Penfold Creek Area near Quesnel Lake, British Columbia. *J. Petrol.* 20,743-94.
- FRASER, D.G. & LAWLESS, P.J. 1978. Palaeogeotherms: implications of disequilibrium in garnet lherzolite xenoliths. *Nature* 273,220-2.
- GANGULY, J. 1972. Staurolite stability and related parageneses: theory, experiments and applications. *J. Petrol.* 13,335-65.
- GANGULY, J. 1979. Garnet and clinopyroxene solid solutions and geothermometry based on Fe-Mg distribution coefficient. *Geochim. Cosmochim. Acta* 42,579-609.
- GANGULY, J. & KENNEDY, G.C. 1974. The energetics of natural garnet solid solutions. *Contrib. Mineral. Petrol.* 48,137-48.
- GANGULY, J. & SAXENA, S.K. 1984. Mixing properties of aluminosilicate garnets: constraints from natural and experimental data and applications to geothermo-barometry. *Am. Mineral.* 69,88-97.
- GARSON, M.S. & PLANT, J. 1973. Alpine type ultramafic rocks and episodic mountain building in the Scottish Highlands. *Nature Phys. Sci.* 242,34-8.
- GHENT, E.D., STOUT, M.Z. 1981a. Geobarometry and geothermometry of plagioclase-biotite-garnet-muscovite assemblages. *Contrib. Mineral. Petrol.* 76,92-7.

- GHENT, E.D. & STOUT, M.Z. 1981b. Metamorphism at the base of the Semail Ophiolite, SE Oman Mountains. *J. Geophys. Res.* 86,2557-72.
- GHENT, E.D., STOUT, M.Z. & RAESIDE, R.P. 1983. Plagioclase-clinopyroxene-garnet-quartz equilibria and the geobarometry and geothermometry of garnet amphibolites from Mica Creek, British Columbia. *Can. J. Earth Sci.* 20,699-706.
- GOLDMAN, D. & ALBEE, A.L. 1977. Correlation of Mg/Fe partitioning between garnet and biotite with $^{18}\text{O}/^{16}\text{O}$ partitioning between quartz and magnetite. *Am. J. Sci.* 277,750-67.
- GOLDSMITH, J.R. 1981a. The melting and breakdown reactions of anorthite at high temperatures and pressures. *Am. Mineral.* 65,272-84.
- GOLDSMITH, J.R. 1981b. The join $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-H}_2\text{O}$ (anorthite-water) at elevated temperatures and pressures. *Am. Mineral.* 66,1183-88.
- GOLDSMITH, J.R. & NEWTON, R.C. 1969. P-T-X relations in the system $\text{CaCO}_3\text{-MgCO}_3$ at high temperatures and pressures. *Am. J. Sci.* 267A,160-90.
- GORDON, T.M. & GREENWOOD, H.J. 1971. The stability of grossularite in $\text{H}_2\text{O-CO}_2$ mixtures. *Am. Mineral.* 56,1674-88.
- GRAHAM, C.M. & BRADBURY, H.J. 1981. Cambrian and late Precambrian basaltic igneous activity in the Scottish Dalradian: a review. *Geol. Mag.* 118, 27-35.
- GRAHAM, C.M., GREIG, K.M., SHEPPARD, S.M.F. & TURI, B. 1983. Genesis and mobility of the $\text{H}_2\text{O-CO}_2$ fluid phase during regional greenschist and epidote amphibolite facies metamorphism: a petrological and stable isotope study in the Scottish Dalradian. *J. geol. Soc. London* 140,577- 600.
- GRAHAM, C.M. & POWELL, R. 1984. A garnet hornblende geothermometer: calibration, testing and application to the Pelona Schist, Southern California. *J. metamorphic Geol.* 2,13-31.
- GRAMBLING, J.A. 1981. Kyanite, andalusite and sillimanite in the Truchas Peaks Region, New Mexico. *Am. Mineral.* 66,702-22.

- GRAMBLING, J.A. 1983. Reversals in Fe-Mg partitioning between chloritoid and staurolite. *Am. Mineral.* 68,373-88.
- GRAMBLING, J.A. 1984. Coexisting paragonite and quartz in sillimanitic rocks from New Maine. *Am. Mineral.* 69,79-87.
- GREEN, D.H. & RINGWOOD, A.E. 1967. An experimental investigation of the gabbro to eclogite transformation and its petrological applications. *Geochim. Cosmochim. Acta* 31,767-837.
- GREENWOOD, H.J. 1967. Wollastonite : stability in H₂O-CO₂ mixtures and occurrence in a contact metamorphic aureole near Salmo, British Columbia Canada. *Am. Mineral.* 52,1669-80.
- GRIFFIN, D.T., GOSNEY, J.C. & PHILLIPS, W.R. 1982. The chemical formula of natural staurolite. *Am. Mineral.* 67,292-7.
- GRESENS, R. 1967. Composition volume relationships of metasomatism. *Chem. Geol.* 2,47-65.
- HALLIDAY, A.N., AFTALION, M., VANBREEMEN, O. & JOCELYN, J. 1979. Petrogenetic significance of Rb-Sr and U-Pb isotopic systems in the 400ma old British Granitoids and their hosts. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British isles-reviewed.* Spec. Publ. geol. Soc. London 8,653-62.
- HAMILTON, P.J., O'NIONS, R.K. & PANKHURST, R.J. 1980. Isotopic evidence for the provenance of some Caledonian granites. *Nature* 287,279-84.
- HANSEN, B. 1981. The transition from pyroxene granulite facies to garnet clinopyroxene granulite facies. Experiments in the CMAS system. *Contrib. Mineral. Petrol.* 76,234-42.
- HARKER, R.I. & TUTTLE, O.F. 1956. Experimental data on the P_{CO₂}-T curve for the reaction calcite + quartz → wollastonite + CO₂. *Am. J. Sci.* 254,239-56.

- HARLEY, S.R. 1984. An experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. *Contrib. Mineral. Petrol.* 86,359-73.
- HARLEY, S.R. & GREEN, D.H. 1982. Garnet-orthopyroxene barometry for granulites and garnet peridotites. *Nature* 300,697-700.
- HARPER, C.T. 1967. The geological interpretation of K-Ar ages of metamorphic rocks from the Scottish Caledonides. *Scott. J. Geol.* 3,128-32.
- HARRIS, A.L., BALDWIN, C.T., BRADBURY, H.J., JOHNSON, H.D. & SMITH, R.A. 1978. Ensialic basin sedimentation: the Dalradian Supergroup. In BOWES, D.R. & LEAKE, B.E. (eds.) *Crustal evolution in northwest Britain and adjacent regions. Geol. J. Spec. Issue* 10,115-38.
- HARRIS, A.L. & FETTES, D.J. 1972. Stratigraphy and structure of the Dalradian rocks at the Highland Border, Scotland. *Scott. J. Geol.* 8,253-64.
- HARRIS, A.L. & PITCHER, W.S. 1975. The Dalradian Supergroup. In HARRIS, A.L. et al. *A correlation of the PreCambrian rocks of the British Isles. Spec. Rep. geol. Soc. London* 6.
- HARTE, B. 1979. The Tarfside succession and the structure and stratigraphy of the eastern Scottish Dalradian rocks. In HARRIS, A.L., [HARTE, B. et al. paper in press, *J. geol. Soc. London*.]
- HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles reviewed. Spec. Publ. geol. Soc. London* 8,221-30.
- HARTE, B. & HUDSON, N.F.C. 1979. Pelite facies series and the temperatures and pressures of Dalradian metamorphism in E Scotland. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.), *The Caledonides of the British Isles-reviewed. Spec. Publ. geol. Soc. London* 8,324-32.
- HARTE, B. & JOHNSON, M.R.W. 1969. Metamorphic history of Dalradian rocks in Glens Clova, Esk and Lethnot, Angus, Scotland. *Scott. J. Geol.* 5,54-80.

- HASELTON, H.T. & NEWTON, R.C. 1980. Thermodynamics of pyrope-grossular garnets and their stabilities at high temperatures and pressures. *J. Geophys. Res.* 85, 6973-82.
- HASELTON, H.T. & WESTRUM, E.F. 1980. Low temperature heat capacities of synthetic pyrope, grossular and pyrope₆₀grossular₄₀. *Geochim. Cosmochim. Acta* 44,701-9.
- HATCHER, R.D. & ODOM, A.L. 1980. Timing of thrusting in the southern Appalachians, USA: model for orogeny? *J. geol. Soc. London* 137,321-7.
- HAYS, J.F. 1967. Lime-alumina-silica. Carnegie Institute Washington Yearbook 65,234-39.
- HAZEN, R.M. & FINGER, L.W. 1978. Crystal structure and compressibility of pyrope and grossular to 60kb. *Am. Mineral.* 63,297-303.
- HEINRICH, C.A. 1983. Kyanite eclogite to amphibolite facies evolution of hydrous mafic and pelitic rocks, Adula Nappe, Central Alps. *Contrib. Mineral. Petrol.* 81,30-38.
- HELGESON, H.C., DELANEY, J.M. NESBITT, H.W. & BIRD, D.K. 1978. Summary and critique of the thermodynamic properties of rock forming minerals. *Am. J. Sci.* 278A,1-229.
- HEMLEY, J.J., MONTOYA, J.W., SHAW, D.R. & LUCE, R.W. 1977. Mineral equilibria in the MgO-SiO₂-H₂O system. II Talc antigorite forsterite anthophyllite enstatite stability relations and some geologic implications in the system. *Am. J. Sci.* 277,353-83.
- HENDERSON, W.G. & ROBERTSON, A.H.F. 1982. The Highland Border rocks and their relation to marginal basin development in the Scottish Caledonides. *J. geol. Soc. London* 139,435-52.
- HENSEN, B.J. & ESSENE, E.J. 1971. Stability of pyrope-quartz in the system MgO-Al₂O₃-SiO₂. *Contrib. Mineral. Petrol.* 30,72-83.
- HENSEN, B.J. & GREEN, D.H. 1973. Experimental study of the stability of cordierite and garnet in pelitic compositions at high pressures and

- temperatures III Synthesis of geological data and experimental applications. *Contrib. Mineral. Petrol.* 38,151-66.
- HEWITT, D.A. 1973. Stability of the assemblage muscovite-calcite-quartz. *Am. Mineral.* 58,785-91.
- HEWITT, D.A. 1975. Stability of the assemblage phlogopite-calcite-quartz. *Am. Mineral* 60,391-7.
- HINXMAN, L.W. & ANDERSON 1915. The geology of mid Strathspey and Strathdearn. *Bull. geol. Surv. Scotland* 74.
- HODGES, K.V. & SPEAR, F.S. 1982. Geothermometry, geobarometry and the Al_2SiO_5 triple point at Mount Moosilauke, New Hampshire. *Am. Mineral.* 67,1118-34.
- HOLDAWAY, M.J. 1971. Stability of andalusite and the aluminium silicate phase diagram. *Am. J. Sci.* 271,97-131.
- HOLDAWAY, M.J. 1978. Significance of chloritoid and staurolite bearing rocks in the Picuris Range, New Mexico. *Bull. geol. Soc. Am.* 89,1404- 30.
- HOLDAWAY, M.J. & LEE, S.M. 1977. Fe-Mg cordierite stability in high grade pelitic rocks based on experimental, theoretical and natural observations. *Contrib. Mineral. Petrol.* 63,175-98.
- HOLLAND, T.J.B. 1979a. High water activities in the generation of high pressure kyanite eclogites of the Tauern Window, Austria. *J. Geol.* 87,1-27.
- HOLLAND, T.J.B. 1979b. Experimental determination of the reaction paragonite \rightarrow jadeite + kyanite + H_2O and internally consistent thermodynamic data for part of the system $Na_2O-Al_2O_3-SiO_2-H_2O$ with applications to eclogites and blueschists. *Contrib. Mineral.Petrol.* 68, 293-301.
- HOLLAND, T.J.B. .1981b. Thermodynamic analysis of simple mineral systems. In NEWTON, R.C., NAVROTSKY, A. & WOOD, B.J. (eds.) *Thermodynamics of*

- minerals and melts. Advances in physical geochemistry vol. 1,19-34. Springer-Verlag, London,
- HOLLAND, T.J.B. & NORRIS, R.J. 1979. Deformed pillow lavas from the Central Hohe Tauern, Austria and their bearing on the origin of epidote banded greenstones. Earth Planet. Sci. Lett. 43,397-405.
- HOLLISTER, L.S. 1969. Metastable paragenetic sequence of andalusite, kyanite and sillimanite, Kwoiek area, British Columbia. Am. J. Sci. 267,352-70.
- HOSCHEK, G. 1973. Die Reaktion phlogopit + calcit + quarz \rightarrow tremolit + kalifeldspat + H₂O + CO₂. Contrib. Mineral. Petrol. 39,231-50.
- HOSCHEK, G. 1974. Gehlenite stability in the system CaO-Al₂O₃-SiO₂-H₂O-CO₂. Contrib. Mineral. Petrol. 47,245-72.
- HOSCHEK, G. 1980. Phase relations of a simplified marly system with application to the western Hohe Tauern (Austria). Contrib. Mineral. Petrol. 73,53-68.
- HOUSEMAN, G.A., MCKENZIE, D.P. & MOLNAR, P. 1981. Convection instability of a thickened boundary layer and its relevance for the thermal evolution of continental convergent belts. J. Geophys. Res. 86,6115-32.
- HSU, K.J. 1979. Thin skinned plate tectonics during neo Alpine orogenesis. Am. J. Sci. 279,353-66.
- HUCKENHOLZ, H.G. HOLZL, E. & LINDHUBER, W. 1975. Grossularite, its solidus and liquidus relations in the system CaO-Al₂O₃-SiO₂-H₂O system up to 10kb. Neues Jahrb. Min. Abh. 124, 1-46.
- HUDSON, N.F.C 1980. Regional metamorphism of some Dalradian pelites in the Buchan area NE Scotland. Contrib. Mineral. Petrol. 73,39-51.
- HUDSON, N.F.C. 1984. paper in press, J. geol. Soc. London
- IKIN, N.P. & HARMON. R.S. 1984. Tectonic history of the ophiolitic rocks of the Highland Border Fracture Zone, Scotland, stable isotope evidence for fluid rock interactions during obduction. Tectonophysics 106,31-48.

- JACOBS, G.K. & KERRICK, D.M. 1981a. Devolatilisation equilibria in H_2O-CO_2 and $H_2O-NaCl$ fluids: an experimental and thermodynamic evaluation at elevated pressures and temperatures. *Am. Mineral.* 66,1135-53.
- JACOBS, G.K. & KERRICK, G.K. 1981b. APL & FORTRAN programs for a new equation of state for H_2O-CO_2 and their mixtures at supercritical conditions. *Comp. Geosci* 7,131-43.
- JACOBSON, C.E. 1983. Complex refolding history of the Pelona, Orcopia and Rand Schists, southern California. *Geology* 11,583-86.
- JOHANNES, W. 1980. Melting and subsolidus reactions in the system $K_2O-CaO-Al_2O_3-SiO_2-H_2O$. *Contrib. Mineral. Petrol.* 74,29-34.
- JOHANNES, W. & GUPTA, L.N. 1982. Origin and evolution of a migmatite. *Contrib. Mineral. Petrol.* 79,114-23.
- JOHNSON, C.A., BOHLEN, S.R. & ESSENE, E.J. 1983. An evaluation of garnet clinopyroxene geothermometry in granulites. *Contrib. Mineral. Petrol.* 84,191-8.
- JOHNSON, M.R.W. 1962. Relations of movement and metamorphism in the Dalradian of Banffshire. *Trans. Edinb. Geol. Soc.* 19,29-64.
- JOHNSON, M.R.W. 1963. Some time relations of movement and metamorphism in the Scottish Highlands. *Geologie Mijnb.* 42,121-42.
- JOHNSON, M.R.W. & FROST, R.T.C. 1977. Fault and lineament patterns in the southern Highlands of Scotland. *Geologie Mijnb.* 56,287-94.
- KASE, H. & METZ, P. 1980. Experimental investigation of the metamorphism of siliceous dolomite IV Equilibrium data for the reaction $Diopside + 3Dolomite \rightarrow 2Forsterite + 4Calcite + 2CO_2$. *Contrib. Mineral. Petrol.* 73,151-59.
- KELLEY, K.K. 1962. Heats and free energies of formation of anhydrous silicates. U.S. Bur. Mines Rept. Inv. 5091,32p.

- KENNEDY, M.J. 1980. Serpentine bearing melange in the Dalradian of Co. Mayo and its significance in the development of the Dalradian basin. *J. Earth Sci. R. Dublin Soc.* 3,117-26.
- KERRICK, D.M. & DARKEN, C.S. 1975. Statistical thermodynamic models for ideal oxide and silicate solid solutions with applications to plagioclase. *Geochim. Cosmochim. Acta* 39,1431-42.
- KERRICK, D.M. & JACOBS, G.K. 1981. A modified Redlich Kwong equation for H₂O-CO₂ mixtures at elevated pressures and temperatures. *Am. J. Sci.* 281,735-67.
- KILINC, I.A. 1979. Melting relations in the quartz diorite-H₂O and quartz diorite-H₂O-CO₂ systems. *Neues Jahrb. Min. Monats.* 62-72.
- KITE, C.E. & STODDARD, E.F. 1984. The Halifax County Complex: Oceanic lithosphere in the E North Carolina Piedmont. *Bull. geol. Soc. Am.* 95,422-32.
- KNELLER, B.C. & LESLIE, A.G. 1984. Amphibolite facies metamorphism in shear zones in the Buchan area, NE Scotland. *J. metamorphic Geol.* 2,83-94.
- KRUPKA, K.M., KERRICK, D.M. & ROBIE, R.A. 1977. High temperature heat capacities of dolomite, talc and tremolite and implications to equilibrium in the siliceous dolomite system. *EOS* 9,1060.
- KWAK, T.A.P. 1971. The selective replacement of the aluminium silicates by white mica. *Contrib. Mineral. Petrol.* 32,193-210.
- LAMBERT, R.J., HOLLAND, C.H. & WINCHESTER, J.A. 1982. A geochemical comparison of the Dalradian Leven Schists and the Scottish Grampian Division Monadhliath Schists of Scotland. *J. geol. Soc. London* 139,71- 84.
- LAMBERT, R. St. J. & MCKERROW, W.S. 1976. The Grampian Orogeny. *Scott. J. Geol.* 12,271-92.

- LAPPIN, M.A. & SMITH, D.C. 1978. Mantle equilibrated orthopyroxene eclogite pods from the basal gneisses in the Selje District, Western Norway. *J. Petrol.* 19,530-84.
- LEAKE, B.E. 1978. Nomenclature of amphiboles. *Min. Mag.* 42,533-63.
- LEAKE, B.E., TANNER, P.W. & SINGH, D., & HALLIDAY, A.N. 1983. Major southward thrusting of the Dalradian rocks of Connemara, western Ireland. *Nature*, 305,210-13.
- LESLIE, A.G. 1984. Field relations in the northeastern part of the Insch mafic igneous mass, Aberdeenshire. *Scott. J. Geol.* 20,215-235.
- LESLIE, A.G. paper in press, *J. geol. Soc. London*
- LIOTTA, J.J. & BOHLEN, S.R. 1984. A new garnet thermobarometer. *EOS* 65,291.
- LONKER, S.W. 1981. The P-T-X relations of the cordierite-garnet-sillimanite-quartz equilibrium. *Am. J. Sci.* 28,1056-90.
- LONKER, S.W. 1983. The hydroxyl content of staurolite. *Contrib. Mineral. Petrol.* 84,36-42.
- MACGREGOR, S.M.A. & ROBERTS, J. Dalradian pillow lavas, Ardwell Bridge, Banffshire. *Geol. Mag.* 100,17-22.
- MAGARITZ, M. & HOFMANN, A.W. 1978. Diffusion of Sr, Ba and Na in obsidian. *Geochim. Cosmochim. Acta* 42,595-605.
- MARTIGNOLE, J. & SISI, J.C. 1981. A geological thermometer, barometer and water fugacity indicator. *Contrib. Mineral. Petrol.* 77,38-46.
- MASON, R. 1984. Inverted isograds at Sulitjelma, Norway, the result of shear zone formation. *J. metamorphic Geol.* 2,77-82.
- MASSONE, H.J., MIRWALD, P.W. & SCHREYER, W. 1981. Experimentelle Überprüfung der Reaktionskurve Chlorit + Quarz → Talk + Disthen im System MgO-Al₂O₃-SiO₂-H₂O. *Fortschr. Mineral.* 59,122-23.
- MAX, M.D. & RIDDIHOUGH, R.P. 1975. Continuation of the Highland Boundary Fault in Ireland. *Geology* 3,206-10.

- McLELLAN, E.L. 1984. Contrasting textures in metamorphic-anatectic migmatites, an example from the Scottish Caledonides. *J. metamorphic. Geol.* 1,241-62.
- METZ, G.A., ANOVITZ, L.M., ESSENE, E.J., BOHLEN, S.R., WESTRUM, E.F. & WALL, V.J. 1983. The heat capacity and phase equilibria of almandine. *EOS* 64,346.
- METZ, P. 1967. Experimentelle Bildung von Forsterit und Calcit aus Tremolit und Dolomit. *Geochim. Cosmochim. Acta* 31,517-32.
- METZ, P. 1976. Experimental investigation of the metamorphism of siliceous dolomites. III Equilibrium data for the reaction: Tremolite + 11Dolomite \rightarrow 8Forsterite + 13Calcite + 9CO₂ + H₂O. *Contrib. Mineral. Petrol.* 58,137-48.
- METZ, P. & PUHAN, D. 1970. Experimentelle Untersuchung der Metamorphose von kieselig dolomitischen Sedimenten. I Die Gleichgewichtsdaten der Reaktion: 3Dolomit + 4Quarz + H₂O \rightarrow Talk + 3Calcit + 3CO₂. *Contrib. Mineral. Petrol.* 26,302-14.
- METZ, P. & PUHAN, D. 1971. Korrektur zur Arbeit "Experimentelle Untersuchung der Metamorphose von kieselig dolomitischen Sedimenten. I Die Gleichgewichtsdaten der Reaktion 3Dolomit + 4Quarz + H₂O \rightarrow Talk + 3Calcit + 3CO₂ für die Gesamtgedruck von 1000, 3000 und 5000 bar. *Contrib. Mineral. Petrol.* 31,169-70.
- MILNES, A.G. & PFIFFNER, O.A. 1977. Structural development of the Intrahelvetic Complex of E Switzerland. *Eclog. geol. Helv.* 70,83-95.
- MIRWALD, P.W. & SCHREYER, W. 1977. Die stabile und metastabile Abbaureaktion von Mg-Cordierit in Talk, Disthen und Quarz und ihre Abhängigkeit vom Gleichgewichtswassergehalt des Cordierits. *Fortsch. Min.* 55,95-7.
- MISRA, K.C. & KELLER, F.B. 1978. Ultramafic bodies in the southern Appalachians : A Review. *Am. J. Sci.* 278,389-418.

- MITCHELL, A.H.G. 1984. The British Caledonides : Interpretation from Cenozoic analogues. *Geol. Mag.* 121,47-51.
- MOHR, D.W. & NEWTON, R.C. 1983. Kyanite staurolite metamorphism in sulfidic schists, Anakeeta Formation, Great Smoky Mountain. *Am. J. Sci.* 283,97-134.
- MOLES, N.R. 1983. Sphalerite composition in relation to deposition and metamorphism of the Foss stratiform Ba-Zn-Pb deposit, Aberfoyle, Scotland. *Min. Mag.* 345,487-500.
- MONGKOLTIP, P. & ASHWORTH, J.R. 1983. Quantitative estimation of an open system symplectite forming reaction: restricted diffusion of Al and Si in coronas around olivine. *J. Petrol.* 24,635-61.
- MUNRO, M. 1970. A reassessment of the younger basic igneous rocks between Huntly and Portsoy based on new borehole evidence. *Scott. J. Geol.* 6,41-52.
- MYSEN, B.O. & GRIFFIN, W.L. 1973. Pyroxene stoichiometry and the breakdown of omphacite. *Am. Mineral.* 58,60-63.
- NAGGAR, N.H. & ATHERTON, M.P. 1970. The composition and metamorphic history of some aluminous silicate bearing rocks from the aureoles of the Donegal Granite. *J. Petrol.* 11,549-89.
- NAVROTSKY, A. & COONS, W.E. 1976. Thermochemistry of some pyroxenes and related compounds. *Geochim. Cosmochim. Acta* 40,1281-88.
- NEWTON, R.C. 1965. The thermal stability of zoisite. *J. Geol.* 73,431- 41.
- NEWTON, R.C. 1966. Some calc silicate equilibrium relations. *Am. J. Sci.* 264,204-22.
- NEWTON, R.C. 1972. An experimental determination of the high pressure stability limits of magnesian cordierite under wet and dry conditions. *J. Geology* 80,398-420.
- NEWTON, R.C. 1983. Geobarometry of high grade metamorphic rocks. *Am. J. Sci.* 283A, 1-28.

- NEWTON, R.C., CHARLU, T.V. & KLEPPA, O.J. 1980. Thermochemistry of the high structural state plagioclases. *Geochim. Cosmochim. Acta* 44,933-41.
- NEWTON, R.C. & HASELTON, H.T. 1981. Thermodynamics of the Garnet-Plagioclase- Al_2SiO_5 -Quartz geobarometer. In NEWTON, R.C., NAVROTSKY, A. & WOOD, B.J. (eds.) *Thermodynamics of Minerals and Melts. Advances in physical geochemistry* vol. 1,131-48. (Springer-Verlag).
- NEWTON, R.C. & PERKINS, D. 1982. Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene-(clinopyroxene)-quartz. *Am. Mineral.* 67,203-22.
- NEWTON, R.C. & WOOD, B.J. 1979. Thermodynamics of water in cordierite and some petrological consequences of cordierite as a hydrous phase. *Contrib. Mineral. Petrol.* 68,391-405.
- OHMOTO, H. & KERRICK, D. 1977. Devolatilisation equilibria in graphitic systems. *Am. J. Sci.* 277,1013-44.
- O'NEILL, H.C. & WOOD, B.J. 1979. An experimental study of Fe-Mg exchange partitioning between garnet and olivine and its calibration as a geothermometer. *Contrib. Mineral. Petrol.* 70,59-70.
- ORVILLE, P.M. 1972. Plagioclase cation exchange equilibria with aqueous chloride solutions. Results at 700°C and 2000 bars in the presence of quartz. *Am. J. Sci.* 272,234-72.
- PANKHURST, R.J. 1970. The geochronology of the basic igneous complexes. *Scott. J. Geol.* 6,83-107.
- PANKHURST, R.J. 1974. Rb-Sr whole rock chronology of Caledonian events in NE Scotland. *Bull. geol. Soc. Am.* 85,345-50.
- PANKHURST, R.J., ANDREWS, J.R., PHILLIPS, W.E.A., SANDERS, I.S. & TAYLOR, W.E.G. 1976. Age and structural setting of the Slieve Gamp Igneous Complex, Co. Mayo, Eire. *J. geol. Soc. London* 132,327-36.

- PANKHURST, R.J. & PIDGEON, R.T. 1976. Inherited isotope systems and the source region prehistory of the Caledonian granites in the Dalradian series of Scotland. *Earth Planet. Sci. Lett.* 31,55-68.
- PANKHURST, R.J. & SUTHERLAND, D.S. 1981. Caledonian granites and diorites of Scotland and Ireland. In SUTHERLAND, D.S. (ed.). *Igneous rocks of the British Isles*. John Wiley, New York.
- PARK, R.G. 1969. Structural correlations in metamorphic belts. *Tectonophysics* 7,323-38.
- PEACOCK, J.D., BERRIDGE, N.G., HARRIS, A.L. & MAY, F. 1968. The geology of the Elgin District. *Mem. geol. Surv. Scotland*.
- PERCIVAL, J.A. 1983. High grade metamorphism in the Chapleau-Foley area, Ontario. *Am. Mineral.* 68,667-86.
- PERKINS, D. 1983. The stability of Mg rich garnet in the system CaO-MgO-Al₂O₃-SiO₂ at 1000°C-1300°C and high pressure. *Am. Mineral.* 68,355-64.
- PERKINS, D., WESTRUM, E.F. & ESSENE, E.J. 1980. The thermodynamic properties and phase relations of some minerals in the system CaO-Al₂O₃-SiO₂-H₂O. *Geochim.Cosmochim. Acta* 44,61-84.
- PHILLIPS, G.A. 1980. Water activity changes across an amphibolite granulite facies transition, Broken Hill, Australia. *Contrib. Mineral. Petrol.* 75,377-86.
- PHILLIPS, W.E.A., STILLMAN, C.J. & MURPHY, T. 1976. A Caledonian plate tectonic model. *J. geol. Soc. London* 132,579-609.
- PIASECKI, M.A.J. 1980. New light on the Moine rocks of the Central Highlands of Scotland. *J. geol. Soc. London* 137,41-59.
- PIASECKI, M.A.J. & VANBREEMEN, O. 1979. The Central Highlands granulites: cover basement tectonics in the Moine. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. *Spec. Publ. geol. Soc. London* 8,139-44.

- PIDGEON, R.J. 1969. Zircon U-Pb ages for the Galway granite and the Dalradian, Connemara, Ireland. *Scott. J. Geol.* 5,375-92.
- PIDGEON, R.T. & AFTALION, M. 1978. Cogenetic and inherited zircon U-Pb systems in granites of Scotland and England. In BOWES, D.R. & LEAKE, B.E. (eds.) *Crustal evolution in northwest Britain and adjacent regions.* *Geol. J. Spec. Issue* 10,183-220.
- PIGAGE, L.C. & GREENWOOD, H.J. 1982. Internally consistent estimates of pressure and temperature: The staurolite problem. *Am. J. Sci.* 282,943-69.
- PORTEOUS, W.G. 1973. Metamorphic index minerals in the eastern Dalradian. *Scott. J. Geol.* 9,29-43.
- POWELL, D., BROOK, M. & BAIRD, A.W. 1983. Structural dating of a Precambrian pegmatite in Moine rocks of northern Scotland and its bearing on the status of the Moravian Orogeny. *J. geol. Soc. London* 140,813-23.
- POWELL, M & POWELL, R. 1977. Plagioclase-alkali feldspar thermometry revisited. *Min. Mag.* 41,253-56.
- POWELL, R. 1978. *Equilibrium thermodynamics in petrology.* Harper-Row, London.
- POWELL, R. 1983. Fluids and melting during upper amphibolite facies conditions. *J. geol. Soc. London* 140,629-34.
- POWELL, R. & EVANS, J.A. 1983. A new geobarometer for the assemblage biotite muscovite chlorite quartz. *J. metamorphic Geol.* 1,331-36.
- PRICE, R.A. 1981. The Cordilleran foreland thrust and foldbelt in the southern Canadian Rocky Mountains. In McCLAY, K.R. & PRICE, N.J. (eds.) *Thrust and nappe tectonics.* *Spec. Publ. geol. Soc. London* 9,427-48.
- PRICE, R.A. & MOUNTJOY, E.W. 1970. Geologic structure of the Canadian Rocky Mountains between Bow and Athabasca Rivers-a progress report. In WHEELER, J.O. (ed.) *The structure of the southern Canadian Cordillera.* *Spec. Publ. geol. Assoc. Canada* 6,7-25.

PUHAN, D. 1978. Experimental study of the reaction $3\text{Dolomite} + \text{K feldspar} + \text{H}_2\text{O} \rightarrow \text{Phlogopite} + 3\text{Calcite} + 3\text{CO}_2$ at the total gas pressures of 4000 and 6000 bars. *Neues Jahrb. Min. Monat.* 3,110-27.

PUHAN, D. & JOHANNES, W. 1974. Experimentelle Untersuchung der Reaktion $\text{Dolomit} + \text{Kalifeldspat} + \text{H}_2\text{O} \rightarrow \text{Phlogopit} + \text{Calcit} + \text{CO}_2$. *Contrib. Mineral. Petrol.* 48,23-31.

RAO, B. & JOHANNES, W. 1979. Further data on the stability of staurolite + quartz and related assemblages. *Neues Jahrb. Mineral. Mh.* 437-47.

RAMSAY, D.M. & STURT, B.A. 1979. The status of the Banff Nappe. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. *Spec. Publ. geol. Soc. London* 8,145-51.

RAMSAY, J.G., CASEY, M. & KLIGFIELD, R. 1983. Role of shear in the development of the Helvetic fold thrust belt of Switzerland. *Geology* 11,439-42.

READ, H.H. 1923. The geology of the country around Banff, Huntly and Turrif. *Memoir geol. Surv. Scotland*.

READ, H.H. 1928a. The Highland Schists of Middle Deeside and east Glen Muick. *Trans. Roy. Soc. Edinb.* 55,755-72.

READ, H.H. 1928b. The igneous and metamorphic history of Cromar, Deeside, Aberdeenshire. *Trans. Roy. Soc. Edin.* 55,317-52.

READ, H.H. 1952. Metamorphism and migmatization in the Ythan Valley, Aberdeenshire. *Trans. Edinb. Geol. Soc.* 15,265-79.

READ, H.H. 1955. The Banff Nappe. an interpretation of the structure of the Dalradian rocks of NE Scotland. *Proc. geol. Ass.* 66,1-29.

READ, H.H. & FARQUHAR, O.C. 1956. The Buchan Anticline of the Banff Nappe of Dalradian rocks in NE Scotland. *Q. J. geol. Soc. london* 112,131-56.

RICHARDSON, S.W. 1968. Staurolite stability in parts of the system Fe-Al-Si-O-H. *J. Petrol.* 9,467-88.

- RICHARDSON, S.W., GILBERT, M.C. & BELL, P.M. 1969. Experimental determination of the kyanite-andalusite and andalusite-sillimanite equilibrium, the aluminosilicate triple point. *Am. J. Sci.* 267,259-72.
- RICHARDSON, S.W. & POWELL, R. 1976. Thermal consequences of Dalradian metamorphism in the central Highlands Scotland. *Scott. J. Geol.* 12,237-68.
- ROBERTS, A.M. & HARRIS, A.L. 1983. The Loch Quoich Line- a limit of early Palaeozoic crustal reworking in the Moine of the northern Highlands of Scotland. *J. geol. Soc. London* 140,883-92.
- ROBERTS, J.L. & SANDERSON, D.J. 1974. Oblique fold axes in the Dalradian rocks of the southwest Highlands. *Scott. J. Geol.* 9,281-96.
- ROBERTS, J.L. & TREAGUS, J.E. 1977. Polyphase generation of nappe structures in the Dalradian rocks. *Scott. J. Geol.* 13,237-48.
- ROBERTS, J.L. & TREAGUS, J.E. 1979. Stratigraphical and structural correlation between the Dalradian rocks of the SW and Central Highlands of Scotland. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. *The Caledonides of the British Isles-reviewed*. *Spec. Publ. geol. Soc. London* 8,199-210.
- ROBIE, R.A. & HEMINGWAY, B.S. 1984. Entropies of kyanite, andalusite and sillimanite: additional constraints on the pressures and temperatures of the Al_2SiO_5 triple point. *Am. Mineral.* 69,298-306.
- ROBIE, R.A., HEMINGWAY, B.S. & FISHER, J.R. 1978. Thermodynamic properties of minerals and related substances at 298.15K and 1bar (10^5 Pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1452.
- ROBIE, R.A., HEMINGWAY, B.S. & TAKEI, H. 1984. Heat capacities and entropies of Mg_2SiO_4 , Mn_2SiO_4 and Co_2SiO_4 between 5 and 380K. *Am. Mineral.* 67,470-82.
- ROBINSON, G.R. 1983. Calibration of the Mu-Bi-Qtz-garnet- aluminosilicate geothermobarometer. *EOS* 64,351.

- RUBIE, D.C. 1984. A thrust tectonic model for high pressure metamorphism and deformation in the Sesia Zone western Alps. *J. Geology* 92,21-36.
- RUMBLE, D. 1973. Andalusite, kyanite and sillimanite from the Mount Moosilauke region New Hampshire. *Bull. geol. Soc. Am.* 84,2423-35.
- RUMBLE, D. 1978. Mineralogy, petrology and oxygen isotopic geochemistry of the Clough Formation, Black Mountain, Western New Hampshire, U.S.A. *J. Petrol.* 19,317-40.
- RUTHERFORD, M.J. 1973. The phase relations of aluminous iron biotites in the system KAlSi_3O_8 - KAlSiO_4 - Al_2O_3 -Fe-O-H. *J. Petrol.* 14,159-80.
- RYAN, P.D., FLOYD, P.A. & ARCHER, J.B. 1980. The stratigraphy and petrochemistry of the Loch Nafoeey Group (Tremadocian), western Ireland. *J. geol. Soc. London* 137,443-59.
- RYAN, P.D., SAWAL, U.K. & ROWLANDS, A.S. 1983. Ophiolitic melange separates ortho and para tectonic Caledonides in western Ireland. *Nature* 302,50-52.
- RYZHENKO, B.N. & VOLKOV, V.P. 1971. Fugacity coefficients of some gases in a broad range of temperatures and pressures. *Geochem. Inter.* 468-81.
- SACK, R.O. 1980. Some constraints on the thermodynamic mixing properties of Fe-Mg orthopyroxenes and olivines. *Contrib. Mineral. Petrol.* 71,237-46.
- SALEEBY, J. & SHARP, W. 1980. Chronology of the structural and petrological development of the SW Sierra Nevada foothills, California, Summary. *Bull. geol. Soc. Am.* 91,317-20.
- SALJE, E. & WERNEKE, CHR. 1982. The phase equilibrium between sillimanite and andalusite as determined from lattice vibrations. *Contrib. Mineral. Petrol.* 79,56-67.
- SALLOMY, J.T. & PIPER, J.D.A. 1973. Palaeomagnetic studies in the British Caledonides. II the younger gabbros of Aberdeenshire, Scotland. *Geophys. J. R. astr. Soc.* 34,13-26.

- SAXENA, S.K. 1973. Thermodynamics of rock forming crystalline solutions. Springer Verlag New York.
- SAXENA, S.K. 1979. Garnet clinopyroxene geothermometer. Contrib. Mineral. Petrol. 70,229-35.
- SAXENA, S.K. & RIBBE, P.H. 1972. Activity composition relationships in feldspars. Contrib. Mineral. Petrol. 37,131-8.
- SCHMID, R. & WOOD, B.J. 1976. Granulite metapelites from the Ivrea Zone. Contrib. Mineral. Petrol. 54,255-79.
- SCHMULOVICH, K.I. & SHMONOV, V.M. 1975. Fugacity coefficients of CO₂ from 1.0132 to 10,000 bars and from 450 to 1300K. Geokhimiya 4,551-5.
- SCHULIEN, S. 1980. Mg-Fe partitioning between biotite and a supercritical chloride solution. Contrib. Mineral. Petrol. 74,85-94.
- SECK, H.A. 1971. Alkalifeldspate und Plagioklase in System NaAlSi₃O₈-KAlSi₃O₈-CaAl₂Si₂O₈-H₂O bei Temperaturen von 650°C bis 900°C. Neues Jahrb. Mineral. Abh. 115,315-45.
- SEIFERT, F. 1970. Low temperature compatibility relations of cordierite in haplopelites of the system K₂O, MgO, Al₂O₃, SiO₂, H₂O. J. Petrol. 11,73-99.
- SHACKELTON, R.M. & RIES, A.C. 1984. The relation between regionally consistent stretching lineations and plate motion. J. Struct. Geol. 3,111-20.
- SHEARER, J.A. & KLEPPA, O.J. 1973. The enthalpies of formation of MgAl₂O₄, MgSiO₃, Mg₂SiO₄, and Al₂SiO₅ by oxide melt solution calorimetry. J. Inorg. Nuclear Chemistry 35,1073-78.
- SINHA-ROY, S. 1982. The Himalayan Main Central Thrust and its implications for Himalayan inverted metamorphism. Tectonophysics 84,197-224.

- SIVAPRAKASH, C. 1982. Geothermometry and geobarometry of Dalradian metapelites and metabasites from the Central Scottish Highlands. *Scott. J. Geol.* 18,109-24.
- SKIPPEN, G.B. 1971. Experimental data for reactions in sileaceous marbles. *J. Geol.* 79,457-81.
- SKIPPEN, G.B. 1974. An experimental model for low pressure metamorphism of sileaceous dolomitic marble. *Am. J. Sci.* 274,487-509.
- SLAUGHTER, J., KERRICK, D.M. & WALL, V.J. 1975. Experimental and thermodynamic study of equilibria in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$. *Am. J. Sci.* 275,143-62.
- SMITH, C.G. 1977. Investigation of stratiform sulphide mineralisation in parts of the Dalradian of Central Perthshire. *Trans. Inst. Min. Met. Soc.* B86,B50-51.
- SMITH, D.I. & WATSON, J. 1983. Scale and timing of movements on the Great Glen Fault Scotland. *Geology* 11,523-6.
- SPEAR, F.S. 1980. $\text{NaSi} \rightarrow \text{CaAl}$ exchange equilibrium between plagioclase and amphibole. *Contrib. Mineral. Petrol.* 72,33-41.
- SPEAR, F.S. 1981a. Amphibole plagioclase equilibria: An empirical model for the relation $\text{Albite} + \text{Tremolite} \rightarrow \text{Edenite} + 4\text{Quartz}$. *Contrib. Mineral. Petrol.* 77,355-64.
- SPEAR, F.S. 1981b. An experimental study of hornblende stability and compositional variability in amphibolite. *Am. J. Sci.* 281,697-734.
- SPEAR, F.S. & SELVERSTONE, J. 1983. Quantitative estimation of P-T paths from zoned minerals: Theory and tectonic applications. *Contrib. Mineral. Petrol.* 183,348-57.
- SPRAY, J.G. & WILLIAMS, G.D. 1980. The subophiolitic rocks of the Ballantrae Igneous Complex, SW Scotland. *J. geol. Soc. London* 137,359-68.

- STEWART, F.H. & JOHNSON, M.R.W. 1960. The structural state of the Younger Gabbros of NE Scotland. *Trans. Edin. Geol. Soc.* 18,104-12.
- STORMER, J.C. 1975. A practical two feldspar geothermometer. *Am. Mineral.* 60,667-74.
- STOUT, J.H. 1972. Phase petrology and mineral chemistry of coexisting amphiboles from Telemark, Norway. *J. Petrol.* 13,99-145.
- STURT, B.A., RAMSAY, D.M., PRINGLE, I.R. & TEGGIN, I.R. 1977. Precambrian gneisses in the Dalradian sequence of NE Scotland. *J. geol. Soc. London* 134,41-4.
- SUTTON, J. & WATSON, J. 1956. The Boyndie Syncline of the Dalradian of the Banffshire Coast. *Q. J. geol. Soc. London* 112,103-30.
- SWEATMAN, J.R. & LONG, J.V.P. 1969. Quantitative electron probe microanalysis of rock forming minerals. *J. Petrol.* 10,322-79.
- TANNER, P. & SHACKELTON, R.M. 1979. Structure and stratigraphy of the Dalradian rocks of the Bennabeola area, Connemara, Eire. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. *Spec. publ. geol. Soc. London* 8,243-56.
- THIRLWALL, M.F. 1981. Implications for Caledonian plate tectonic models of chemical data from volcanic rocks of the British Old Red Sandstone. *J. geol. Soc. London* 138,139-45.
- THOMAS, P.R. 1979. The Central Highland Root Zone. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. *Spec. Publ. geol. Soc. London* 8,205-11.
- THOMPSON, A.B. 1976. Mineral reactions in some pelitic rocks II Calculations of some P-T-X (Fe-Mg) phase relations. *Am. J. Sci.* 276,425-54.
- TILLEY, C.E. 1924. The facies classification of rocks. *Geol. Mag.* 61,167-71.

- TILLEY, C.E. 1925. A preliminary survey of the metamorphic zones in the southern Highlands of Scotland. *Q. J. geol. soc. London* 81,100-12.
- TOBISCH, O.T. & FISKE, R.S. 1982. Repeated parallel deformation in parts of the eastern Sierra Nevada, California and its implications for dating structural events. *J. Struct. Geol.* 4,177-95.
- TORGESON, D.R. & SAHAMA, T.G. 1948. A hydrofluoric acid solution calorimeter and the determination of the heats of formation of Mg_2SiO_4 , $MgSiO_3$ and $CaSiO_3$. *Am. Chem. Soc. Jour.* 70,2156-60.
- TRACY, R.J. & ROBINSON, P. 1980. Evolution of metamorphic belts : information from detailed petrologic studies. In WONES, D.R. (ed.) *Proceedings " the Caledonides of the U.S.A."* Virginia poly. Inst. & State Univ. Mem 2,189-96.
- TREAGUS, J.E. & ROBERTS, J.R. 1981. The Boyndie Syncline, a D1 structure in the Dalradian of Scotland. *Geol. J.* 16,125-35.
- TRELOAR, P.J. 1981. Garnet biotite cordierite thermometry and barometry in the Cashel thermal aureole, Connemara, Ireland. *Min. Mag.* 44,183-9.
- TURNELL, H.B. & BRIDEN, J.C. 1983. Palaeomagnetism of NW Scotland syenites in relation to local and regional tectonics. *Geophys. J. R. Astr. Soc.* 75,217-34.
- TYLER, I.M. & ASHWORTH, J.R. 1982. Sillimanite-potash feldspar assemblages in graphitic pelites, Strontian area, Scotland. *Contrib. Mineral. Petrol.* 81,18-29.
- TYLER, I.M. & ASHWORTH, J.R. in press. The metamorphic environment of the Foyers Complex. *Scott. J. Geol.*
- UYEDA, S. & KANAMORI, H. 1979. Back arc opening and the mode of subduction. *J. Geophys. Res.* 84,1049-61.
- VANBREEMEN, O., AFTALION, M. & JOHNSON, M.R.W. 1979a. Age of the Loch Borrolan Complex, Assynt and late movements along the Moine Thrust Zone. *J. geol. Soc. London* 136,489-95.

- VAN BREEMEN, O., AFTALION, M., PANKHURST, R.J. & RICHARDSON, S.W. 1979b. Age of the Glen Dessary Syenite, Invernessshire, diachronous Palaeozoic metamorphism across the Great Glen. *Scott. J. Geol.* 15,49-62.
- VAN BREEMEN, O. & BOYD, R. 1972. A radiometric age for a pegmatite cutting the Belhelvie mafic intrusion, Aberdeenshire. *Scott. J. Geol.* 8,115-20.
- VAN BREEMEN, O. & PIASECKI, M.A.J. 1983. The Glen Kyllachy Granite and its bearing on the nature of the Caledonian Orogeny in Scotland. *J. geol. Soc. London* 140,47-62.
- VAN BREEMEN, O. & PIDGEON, R.T. 1974. Precambrian and Palaeozoic pegmatites in the Moines of N Scotland. *J. geol. Soc. London* 130,493-507.
- VAN DER VOO, R. & SCOTESE, C.R. 1981. Palaeomagnetic evidence for a large (~2000km) offset along the Great Glen Fault during the Carboniferous. *Geology* 9,583-89.
- VERNON, R.H. 1978. Porphyroblast matrix microstructural relationships in deformed metamorphic rocks. *Geol. Rund.* 67,288-305.
- VERNON, R.H. 1979. Formation of late sillimanite by hydrogen metasomatism (base leaching) in some high grade gneisses. *Lithos* 12,143- 52.
- VERNON, R.H. & FLOOD, R.H. 1977. Interpretation of metamorphic assemblages containing fibrolitic sillimanite. *Contrib. Mineral. Petrol.* 59,227-35.
- WATKINS, K.P. 1984. The structure of the Balquhider-Crianlarich region of the Scottish Dalradian and its relation to Barrovian isograd surfaces. *Scott. J. Geol.* 20,53-64.
- WATSON, J. 1964. Conditions in the metamorphic Caledonides during the period of late orogenic cooling. *Geol. Mag.* 101,457-65.
- WEEKS, W.F. 1956. Heats of formation of metamorphic minerals in the system CaO-MgO-SiO₂-H₂O and their petrological significance. *J. Geology* 64,456-72.

- WELLS, P.R.A. 1979a. P-T conditions in the Moines of the Central Highlands, Scotland. *J. geol. Soc. London* 136,663-71.
- WELLS, P.R.A. 1979b. Chemical and thermal evolution of Archaean sialic crust, SW Greenland. *J. Petrol.* 20,187-226.
- WELLS, P.R.A. 1980. Thermal models of the magmatic accretion and subsequent metamorphism of continental crust. *Earth Planet. Sci. Lett.* 46,253-65.
- WELLS, P.R.A. 1983. Reply to discussion of WELLS, P.R.A. 1979. *J. geol. Soc. London* 138,206-9.
- WELLS, P.R.A. & RICHARDSON, S.W. 1979. Thermal evolution of metamorphic rocks in the Central Highlands of Scotland. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) *The Caledonides of the British Isles-reviewed*. Spec. Publ. *geol. Soc. London* 8,339-45.
- WILLIAMS, P.F. & ZWART, H.F. 1977. A model for the formation of the Seve-Koli Nappe complex. In SAXENA, S.K. & BHATTACHARJI, S. 1977. *Energetics of geological processes*. Springer Verlag, New York. 169-87.
- WINCHESTER, J.A. 1974. The zonal pattern of regional metamorphism in the Scottish Caledonides. *J. geol. Soc. London* 130,509-24.
- WINCHESTER, J.A. 1983. Discussion of WELLS, P.R.A. 1979. *J. geol. soc. London* 138,205-6.
- WINDOM, K.E. & BOETTCHER, A.L. 1976. The effect of reduced activity of anorthite on the reaction grossular + quartz \rightarrow anorthite + 2wollastonite: a model for plagioclase in the earths crust and upper mantle. *Am. Mineral.* 61,889-96.
- WINKLER, H.G.F. 1974. *Petrogenesis of metamorphic rocks*. 5th edition. Springer-Verlag, New York.
- WISEMAN, J.D.H. 1934. The Central and Southwest Highlands Epidiorites : A study in progressive metamorphism. *Q. J. geol. Soc. London* 90,354- 415.

- WONES, D.R. & DODGE, F.C. 1966. On the stability of phlogopite (abs.). Geol. Soc. Am. spec. Paper 101,242-62.
- WOOD, B.J. 1978. reactions involving anorthite and $\text{CaAl}_2\text{SiO}_6$ pyroxene at high pressures and temperatures. Am. J. Sci. 278,930-42.
- WOOD, B.J. 1979. Activity composition relationships in $\text{Ca}(\text{M},\text{F})\text{Si}_2\text{O}_6$ -CaTs solid solutions. Am. J. Sci. 279,854-75.
- WOOD, B.J. & BANNO, S. 1973. Garnet-orthopyroxene-clinopyroxene relationships in simple and complex systems. Contrib. Mineral. Petrol. 42,109-24.
- WOOD, B.J. & HOLLOWAY, J.R. 1984. A thermodynamic model for subsolidus equilibria in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. Geochim. Cosmochim. Acta 48,159-76.
- YARDLEY, B.W.D. 1976. Deformation and metamorphism of Dalradian rocks and the evolution of the Connemara Cordillera. J. geol. Soc. London 132,521-42.
- YARDLEY, B.W.D. 1977. Nature and mechanism of sillimanite growth in the Connemara Schists, Ireland. Contrib. Mineral. Petrol. 65,53-8.
- YARDLEY, B.W.D. 1978. Genesis of the Skagit migmatite, Washington and the distinction between possible mechanisms of migmatization. Bull. geol. Soc. Am. 89,941-51.
- YARDLEY, B.W.D. 1981. A note on the composition and stability of Fe staurolite. Neues Jahrb. Miner. Monat. 127-32.
- YARDLEY, B.W.D., LEAKE, B.E. & FARROW, C.M. 1980. The metamorphism of Fe rich pelites from Connemara, Ireland. J. Petrol. 21,365-99.
- YARDLEY, B.W.D., LONG, C.B. & MAX, M.D. 1979. Patterns of metamorphism in the Ox Mountains and adjacent parts of western Ireland. In HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds.) The Caledonides of the British Isles reviewed. Spec. Publ. geol. Soc. London 8,369-74.

YARDLEY, B.W.D. & SENIOR, A. 1982. Basic magmatism in Connemara, Ireland evidence for a volcanic arc. *J. geol. Soc. London* 139,67-70.

YARDLEY, B.W.D., VINE, F.J. & BALDWIN, C.J. 1982. The plate tectonic setting of NW Britain and Ireland in late Cambrian and early Ordovician times. *J. geol. Soc. London* 139,457-66.

YODER, H.S. 1967. Albite-anorthite-quartz-H₂O at 5kb. *Carnegie Institute, Washington Yearbook* 66,477-8.

ZIEGENBEIN, P. & JOHANNES, W. 1974. Wollastonitbildung aus Quarz und Calcit bei P=2,4 und 6kb. *Forsch. Min.* 52,77-79.

APPENDIX A

MINERAL ASSEMBLAGES AND PETROGRAPHIC DATA

This appendix comprises a list of assemblages and locations with some petrographic notes for selected rocks from those studied in thin section.

GLENBUCHAT AREA (close to the NW margin of the Morven Cabrach Gabbro 1A&1B (NJ335196)

Garnet-staurolite-biotite-muscovite-quartz-opaques.

The muscovite-biotite schistosity is deflected around porphyroblast phases.

4A (N0331208)

Andalusite-biotite-muscovite-quartz-opaques.

The andalusites have been replaced post deformationally by white mica. Replaced andalusites contain quartz inclusion trails which are oblique to the external schistosity.

5 (N0332108)

Chlorite-biotite-muscovite-quartz-opaques.

Large rectangular porphyroblasts have been replaced post deformationally by white mica. These were presumably andalusite by analogy with 4A.

N OF GLEN AVON

21 (NJ214266), 23 (NJ248320) and 25 (NJ228307)

These rocks contain the maximum assemblage staurolite-garnet-biotite-muscovite-plagioclase-quartz-opaques. The staurolites are syntectonic, containing inclusion trails which are gently crenulated, compared to an intensely folded schistosity external to the porphyroblasts.

19A (NJ152207)

Kyanite-staurolite-garnet-biotite-muscovite-quartz-plagioclase-opaques. Staurolites are syntectonic. Plagioclase and chlorite both overgrow the schistosity.

RIVER BLACKWATER (NW of Morven Cabrach)

946A (NJ374307)

Andalusite-plagioclase-biotite-muscovite-quartz-opaques.

Andalusites are syntectonic.

946C (NJ374307)

Garnet-epidote-amphibole-biotite-calcite-quartz-sphene-opaques.

948 (NJ361304)

Andalusites are pre to syntectonic. In their centres they include fine randomly orientated biotite, muscovite and quartz. Edges include coarse muscovites and biotites, defining a rotated inclusion trail, continuous with the external schistosity. Two phases of andalusite growth may be represented.

949 (NJ362304)

Gt-Bi-Mu-Qtz-opaques

952A (NJ333232)

Garnet-zoisite-plagioclase-hornblende-clinopyroxene.

A quartz absent garnet-cpx assemblage. Other metapelitic hornfels occur around this location, to the immediate west of the Morven Cabrach intrusion.

GLEN SHEE

916B/C (N0118805)

Garnet-muscovite-biotite-chlorite-quartz-rutile

Fine muscovite biotite schistosity. Chlorite is texturally late.

915A/B (N0124814)

Garnet-biotite-muscovite-chlorite-quartz-rutile-opaques-plagioclase

Chlorite texturally late.

731A (N0181724)

Garnet-biotite-muscovite-quartz-opaques.

Very deformed texture.

733 (N0178762)

Garnet-staurolite-biotite-muscovite-quartz-opaques-chlorite

Staurolite includes an early schistosity. Small amounts of chlorite are texturally late.

AMPHIBOLITES IN THE SCHICHALLION AREA

Most amphibolites studied from this area contain the basic assemblage garnet-hornblende-plagioclase-quartz-sphene-opaques. Plagioclase typically rims garnets. More deformed rocks tend not to have these coronas. In addition many rocks have preserved igneous textures. A brief summary of some occurrences follows: (all contain the basic assemblage above).

746B (NN722578) with late scapolite and zoisite

740 (NN773547) epidote and plagioclase replace garnet

752 (NN670590) & 749 (NN715665)-strongly resorbed garnets. Many samples contain biotite and/or late chlorite

747 (NN715667) garnets replaced by plagioclase and calcite. often centres are replaced while rims are intact.

GLEN EY

Rocks have been collected from Glen Ey from the area between N0087883 and N0060093. Broadly speaking pelitic rocks are of two major types. The first is chlorite bearing, but does not contain muscovite. The second contains muscovite, garnet and often kyanite. Staurolite is absent from the area. Maximum assemblages from these types are:

Type 1

Garnet-chlorite-biotite-quartz-plagioclase-opaques-margarite-kyanite

Type 2

Garnet-kyanite-biotite-muscovite-plagioclase-quartz-rutile-ilmenite

In AFM assemblages garnets are often very small with cores containing graphitic inclusions. Large kyanite porphyroblasts overgrow and include

these garnets. Thin sections usually show evidence of more than one phase of deformation. An early very fine muscovite-biotite schistosity is often intensely deformed. Many kyanites are post tectonic (with respect to phases of deformation, visible in one thin section. Others are kinked and internally disrupted. Others show internal inclusion trails, indicating rotation of the kyanites at some later stage. Plagioclase porphyroblasts are relatively late in that they include deformed graphite and mica inclusion trails, continuous with the external schistosity.

Margarite is found to occur quite commonly. It may occur as a retrogressive product, forming rims together with muscovite around kyanite. In Glen ey kyanite is frequently converted to pseudomorphs of margarite-plagioclase-chlorite. These pseudomorphs are preserved within late plagioclase porphyroblasts. Some rocks contain a margarite schistosity. This is usually included within large plagioclase porphyroblasts, but in some rocks the margarite appears to coexist with quartz. The stability of margarite + quartz limits temperatures to 550°C at about 7kb (Chatterjee,1976).

GLEN AVON

Rocks are graphitic micaschists with a fine muscovite-biotite schistosity. Many lithologies contain zoisite. Garnets are syntectonic. Staurolites show evidence of having been rotated after growth (inclusion trails oblique to the external schistosity). Kyanite is late to post tectonic. In some thin sections small microfolding postdates kyanite growth (external crenulated schistosity, internal straight schistosity). In other instances no deformation postdating kyanite growth is detectable. Details of some of the assemblages present follows:

27 (NJ178086)

A/C/F

Garnet-chlorite-biotite-muscovite-quartz-plagioclase-rutile.

Chlorites are texturally late.

B contains staurolite and kyanite in addition to the above.

D: Garnet-biotite-chlorite-quartz-tremolite-plagioclase-calcite.

29 (NJ176087)

A: Muscovite-calcite-quartz.

B: Garnet-chlorite-muscovite-biotite-quartz-zoisite-plagioclase.

Chlorite is late. Biotite occurs within the schistosity and as large porphyroblasts.

30A (NJ176088)

Muscovite-biotite-chlorite-plagioclase-quartz

Shimmer aggregate pseudomorphs are present.

31C (NJ164114)

Garnet-staurolite-biotite-muscovite-quartz-opaques

33B (NJ183062)

Garnet-muscovite-biotite-zoisite-quartz-rutile-opaques

Zoisites overgrow the schistosity.

37A-F (NJ178086)

Kyanite-staurolite-garnet-biotite-muscovite-quartz-opaques-rutile

More than one phase of deformation present.

41A (NJ174088)

Kyanite-staurolite-garnet-biotite-muscovite-paragonite-plagioclase-quartz-rutile-ilmenite

Fine mu-bi schistosity with later biotite porphyroblasts. staurolites contain quartz inclusion trails discontinuous with the external schistosity.

50A (NJ164116)

Zoisite-quartz-biotite-muscovite-calcite-opaques

Zoisite occurs as porphyroblasts

ZZZ (NJ182060)

Kyanite-staurolite-garnet-biotite-muscovite-plagioclase-quartz-rutile-ilmenite.

AILNACK GORGE

Kyanite has not been found coexisting with primary white mica. Secondary white mica, either margarite (see Chinner, 1974) or muscovite may coexist with kyanite. Garnet-chlorite AFM assemblages appear to occur in the area. In most rocks chlorite is a product of the retrogressive reaction of garnet. However in some rocks garnets are relatively fresh and chlorite occurs within the schistosity, parallel to small muscovites and kyanites (91A, 90A, 66A). The chlorite is not directly replace of biotite, as is often the case with kyanite zone rocks. Zoisite-kyanite assemblages have not been found.

Some rocks contain porphyroblasts that have been replaced by white mica during continuing deformation. White mica within the porphyroblast has been deformed to produce a schistosity, oblique to the external schistosity. This new schistosity has then been folded. A list of the more interesting assemblages follows.

54A (NJ156162)

Garnet-zoisite-biotite-chlorite-calcite-quartz-opaques

Zoisites are included in large biotite porphyroblasts, about which the schistosity is deflected.

58A (NJ146151)

Garnet-biotite-calcite-quartz-rutile

60A (NJ145149)

Garnet-biotite-muscovite-chlorite-plagioclase-chlorite

61A (NJ145149)

Biotite-plagioclase-quartz-calcite-opaques

62A (NJ142145)

Garnet-muscovite-biotite-chlorite-quartz-opaques

The rock contains porphyroblasts, replaced by white mica syndeformationally, as described above. Chlorite is late.

66A (NJ140144)

Garnet-biotite-chlorite-quartz-calcite-muscovite-plagioclase-opaques

Chlorite occurs within the schistosity

71A (NJ137138)

Garnet-muscovite-biotite-chlorite-calcite-quartz-opaques

Chlorite late.

73B (NJ129120)

Garnet-kyanite-quartz-biotite-muscovite

Muscovite is late (possibly also margarite)

73A (NJ129120)

Kyanite-biotite-muscovite-chlorite-quartz-plagioclase

Muscovite and chlorite are texturally late.

90A (NJ133124)

Garnet-chlorite-muscovite-biotite-quartz-calcite-opaques-plagioclase

Shimmer aggregate replaces an unknown porphyroblast phase.

91 (NJ132123)

Garnet-chlorite-muscovite-plagioclase-quartz-opaques

Chlorite lies within the foliation and rims garnet. Possible garnet-chlorite assemblage.

96A (NJ129120)

Garnet-kyanite-plagioclase-quartz-muscovite-biotite-chlorite-rutile

Kyanites are rimmed by shimmer aggregate. Muscovite, chlorite and biotite are late, crosscutting and randomly orientated.

DONSIDE

599 (NJ506154) & 600 (NJ482150)

Andalusite-fibrolite-biotite-quartz-muscovite-plagioclase

Several andalusite bearing specimens contain andalusite replaced by large porphyroblastic muscovite, sometimes totally. Most rocks do not contain muscovite, except within the pseudomorphs. Fibrolite is concentrated around the margins of the pseudomorphs or grows on biotite throughout the rock.

INZIE HEAD GNEISSES

602D (NK037657)

Muscovite-biotite-fibrolite-quartz

Many randomly orientated micas with included fibrolite. Exsolved opaques, associated with biotite grain boundaries. A very retrogressed texture.

603K (around NK057633)

Sillimanite-muscovite-biotite-quartz

Prismatic sillimanite, surrounded by shimmer aggregate and randomly orientated micas. Much shimmer aggregate. All micas are randomly orientated.

603I/G (GR as above)

Biotite-plagioclase-quartz-cordierite-chlorite-muscovite

Coarse retrogressed gneisses. Late muscovite and chlorite. Cordierites are now replaced by shimmer.

Generally gneisses from this are are not fresh and are strongly retrogressed.

DUCHRAY HILL GNEISS

Rocks are migmatitic gneisses, usually with muscovite in the SE part of the Duchray Hill Gneiss. Garnets are often elongate within the

schistosity. All the rocks collected are muscovite bearing. Some contain late fibrolite.

Grid References

637 N0185685

638 N0190713

GLEN CLOVA

Metapelitic rocks contain the maximum assemblage :

Kyanite-fibrolite-garnet-staurolite-biotite-muscovite-plagioclase-quartz-rutile-ilmenite-sulphides. Kyanites are embayed and surrounded by muscovite. Fibrolite is commonly included within muscovite. Rocks generally have equilibrium textures and deformation is relatively slight.

Grid References

129 N0315745

135 N0324746

141 N0324746

155 N0315776

Amphibolites in Glen Clova-Duchray Hill Gneiss

In the kyanite zone of this area amphibolites are usually gneissose. The typical assemblage is garnet-hornblende-plagioclase-quartz-opaques. In the northern part of the Duchray Hill Gneiss some rocks contain clinopyroxene in addition to the above assemblage:

807 (N0237775), 809 (N0234772), 811A (N0231779) and 737A (N0230734).

The former three are similar texturally to the Glen Muick metabasites. The latter contains a disequilibrium assemblage and is described in chapter 2. Other rocks nearby this occurrence contain clinopyroxene without garnet. In Glen Clova one amphibolite (727 N0334740) contains the assemblage:

garnet-gedrite-hornblende-chlorite-plagioclase-quartz-biotite-opaques.

GLEN ESK

Rocks studied are coarse schists with muscovite and biotite.

Staurolite is present in some. 648A contains fibrolite and staurolite. The staurolite does not appear to overgrow the fibrolite.

Grid References

647 N0387803

648 N0440785

645 N0413796

An amphibolite 644A (N0428825) contains hornblende-epidote-plagioclase-quartz-opaques-sphene. However round areas, composed of plagioclase, sieved with epidote suggest that garnets may once have been present. Similar textures occur in garnet amphibolites 721A (N0423825-loose) and (N0440805- in situ). 721A does contain some relict garnet.

GLEN MARK

(Sillimanite zone to the south of Glen Muick).

Lithologies comprise migmatized pelites, psammitic rocks and amphibolites. Migmatized metapelites may be of the oligoclase porphyroblast schist type (see chapter 3) e.g. near Craig Michael. Around Craig Michael rocks contain bladed pseudomorphs, now composed of muscovite, inferred to be after kyanite.

812 (N0305783)

Garnet-biotite-muscovite-plagioclase-quartz-opaques-cordierite

Biotite and cordierite replace garnets. This is presumed to be the result of contact metamorphism from the Lochnagar Newer Granite.

813 (N0307783) & 814 (N0305789)

Garnet-hornblende-plagioclase-quartz-opaques-sphene

Garnets are replaced by plagioclase and biotite-the effects of contact metamorphism ?

816A (N0389834)

Garnet-chlorite-muscovite-biotite-plagioclase-quartz-opaques-fibrolite
Relatively fresh and sheared texture. Fibrolite, muscovite and chlorite lie within the foliation. Shimmer aggregate is associated with fibrolite. Muscovite and chlorite are associated with late opaques.

817A (N0394834)

Garnet-chlorite-muscovite-biotite-plagioclase-quartz-opaques
Muscovite and chlorite lie within the foliation.

816B (N0389834) & 829 (N0380839)

Garnet-hornblende-plagioclase-quartz-opaques
Garnet amphibolites with relatively deformed textures compared to those in Glen Muick.

827A (N0385838)

Fibrolite-muscovite-biotite-plagioclase-quartz-opaques
Muscovite pseudomorphs after kyanite. Fibrolite is included within late porphyroblastic muscovite. (see chapter 4)

867A (N0363852) & 865 (N0358872)

Garnet-muscovite-biotite-fibrolite-plagioclase-quartz-opaques
Muscovite generally within the schistosity. In more deformed areas much shimmer aggregate is developed.

870 (N0363852)

Garnet-biotite-muscovite-plagioclase-quartz-opaques
Psammite with muscovite within schistosity. Muscovite pseudomorphs after kyanite nearby.

961 (N0374860)

Hornblende-plagioclase-quartz-sphene-rutile

Sphene rims rutile

955A (N0367852) & 956 (N0367853)

Garnet-muscovite-biotite-plagioclase-sillimanite-quartz-opaques

Porphyroblastic muscovite crosscuts the schistosity. Late shimmer aggregate is associated with fibrolite. Fibrolite often associated with biotite. Large fibrolite mats are included within crosscutting muscovite. Opaques rim biotites.

MARYCULTER

N0852994

MC4 and MC5: retrogressed andalusite and fibrolite bearing metapelites.

MC2 is a garnet amphibolite with:

garnet-hornblende-plagioclase-quartz-sphene-opaques

DEESIDE: CROMAR

Craig Dhu

NJ4901

On the hill of Craig Dhu amphibolites occur similar to garnet-clinopyroxene bearing amphibolites, described from E. Glen Muick. They contain the assemblage hornblende-plagioclase-quartz-opaques. many specimens also contain metamorphic clinopyroxene. Garnet has not been found in association with clinopyroxene, although it is reported by Read (1928).

CRAIG FERRAR (N04999)

The hill is composed of pelitic migmatites with some more psammitic compositions. Granitic segregations are common. The maximum assemblage in melanosomes is:

garnet-andalusite-staurolite-chlorite-muscovite-biotite-plagioclase-quartz opaques-fibrolite. Minor cordierite is present in some rocks. This maximum assemblage is interpreted as disequilibrium and the result of retrogressive reactions in sillimanite gneisses. Feldspars are often

completely replaced by mica, leaving a mica rich rock. Muscovite occurs as late randomly orientated porphyroblasts or as shimmer aggregate. Late biotite, muscovite and chlorite are associated with abundant opaques. Chlorite pools, staurolite and andalusite overgrow the late micas and opaques. Fibrolite trails, continuous with external trails are included within andalusite. Garnets are irregular, but not fractured or extensively resorbed.

DINNET HOUSE (N0450980)

Rocks from the northeast of Dinnet House comprise boulders of variably deformed migmatitic gneiss. The maximum assemblage is:

garnet-plagioclase-sillimanite-biotite-quartz-opaques-cordierite-andalusite. Garnets are extensively resorbed and replaced by biotite aggregates. Feldspars may be replaced by white mica. DH6 contains fresh cordierite and hornfelsic biotite. It has presumably suffered the effects of contact metamorphism. Andalusites may overgrow garnets and prismatic sillimanites. Biotites are often associated with opaques, which may be included or lie along the grain boundaries.

SCAR HILL AREA

The area around Scar hill-

Scar Hill NJ482014

Mullochdhu NJ472006

Hill N of Balnacraig NJ477008

is composed of various migmatitic gneisses, including oligoclase porphyroblast types and coarse xenolithic gneisses. Gneisses may include psammitic, pelitic and metabasic xenoliths. The freshest gneisses from the hill, north of Balnacraig are sillimanite K feldspar gneisses, containing garnet-sillimanite-K feldspar-plagioclase-biotite-quartz-rutile-ilmenite. Retrogressed gneisses contain andalusite and muscovite and garnets are resorbed. These rocks are further described in chapter 4.

844A (N0318894)

Garnet-cordierite-sillimanite-plagioclase-quartz-biotite-muscovite

Garnets are replaced by cordierite and sillimanite is surrounded by late muscovite. In hand specimen the rock is a coarse migmatitic gneiss.

846A (N0328945)

Cordierite-andalusite hornfels

506 (N0328943)

Garnet-cordierite-plagioclase-biotite-quartz-opaques

Hornfels

Calcsilicate lithologies

848C (N0328946)

Garnet-tremolite-plagioclase-quartz-opaques

836A & 481 (N0316936)

Tremolite-phlogopite-calcite-plagioclase-garnet-sphene

Distinctive rock with large radiating tremolites.

Glen Gironck Metabasites

In Glen Gironck metabasites do not contain garnet or clinopyroxene. Metagabbros contain Hornblende-plagioclase-quartz-opaques (e.g. 861 N0329914 & 862 N0330918). A hornblende rock occurs on the hill of Craig Megen (842: N0317897). Many amphibolites on this hill are two amphibole bearing. 526 (N0316904) contains hornblende-cummingtonite-plagioclase-quartz-opaques. Cummingtonite occurs as fibrous aggregates which appear to be pseudomorphous after another amphibole. To the north 518 (N0304927) also contains this assemblage. Other typical assemblages are hornblende plagioclase-quartz-opaques and epidote-hornblende-plagioclase-quartz-opaques in epidote banded amphibolites.

GLEN MUICK (Locations are also shown in the figure)

Hare Cairn/Upper Glen Tanar

410A (N0385883)

Sillimanite-muscovite-biotite-quartz-opaques

Randomly orientated muscovite and biotite porphyroblasts. Fine prismatic sillimanites included in muscovite. Sillimanite aggregate pseudomorph after kyanite (see chapter 4)

454A (N0387887)

Andalusite-muscovite-biotite-quartz-opaques

Some muscovite is aligned within the foliation. Fine shimmer and some porphyroblastic muscovite crosscuts. Andalusite lies within the foliation.

457B (N0385884)

Biotite-muscovite-quartz-plagioclase-opaques

Deformed texture, within which muscovite is aligned.

563B (N0387886)

Sillimanite-andalusite-muscovite-biotite-quartz-opaques

Large amounts of porphyroblastic muscovite and biotite. Sillimanite pseudomorph after kyanite with later andalusite (see chapter 4)

879B (around N0378880)

Garnet-chlorite-muscovite-plagioclase-quartz-fibrolite

Deformed retrogressed gneiss. Muscovite and chlorite postdate the deformation

559/560/DCAB (N0349888)

Andalusite-garnet-sillimanite-biotite-quartz-plagioclase-muscovite-opaques

Fibrolite mats and aggregates of fine prismatic sillimanites. Some rocks are very rich in sillimanite. Andalusite and occasionally cordierite overgrow fibrolite crenulations and trails (see chapter 4)

350A (N0386933)

Garnet-sillimanite-plagioclase-biotite-cordierite-muscovite-opaques

Cordierite replaces garnets and muscovites plagioclase

351A (N0385935)

Garnet-sillimanite-plagioclase-quartz-opaques-biotite-cordierite

546A (N0351873)

Quartz-opaques

Strongly deformed mylonitic quartzite

566A/B/C (N0395933)

Andalusite hornfelses with cordierite forming reaction rims between regional biotite and sillimanite.

Cairn Leuchan Area

430A/B/C (N0387920)

Garnet-sillimanite-biotite-plagioclase-K feldspar-quartz-rutile-ilmenite

Very fresh rock (see chapter 3)

CL (around 3891)

A number of rocks contain assemblages similar to 430A. Some do not contain K feldspar. Most contain rutile, sometimes with ilmenite. Some are very sillimanite rich. Prismatic sillimanites are often deformed around garnet.

432 (N0390925)

Biotite-plagioclase-quartz-cordierite

Very retrogressed rock-a hornfels?

West Glen Muick

415A (N0330894)

Garnet-biotite-plagioclase-quartz-opaques.

Retrogressive staurolite and hercynite overgrowths on magnetite are found.

859A (N0330990)

Garnet-plagioclase-quartz-biotite-opaques. There is much late porphyroblastic muscovite, shimmer aggregate. Garnets are replaced by cordierite.

860A (N0330908)

as 859A

861B (N0329914)

Garnet-chlorite-muscovite-quartz-plagioclase-opaques. Muscovite and chlorite are parallel to the foliation.

882B (N0330894)

as 859A

924A/B/C/D (N0330906)

Garnet-sillimanite-biotite-plagioclase-quartz-opaques. Fresh prismatic sillimanite, no fibrolite. Garnets are resorbed and fractured.

938A (N0331935)

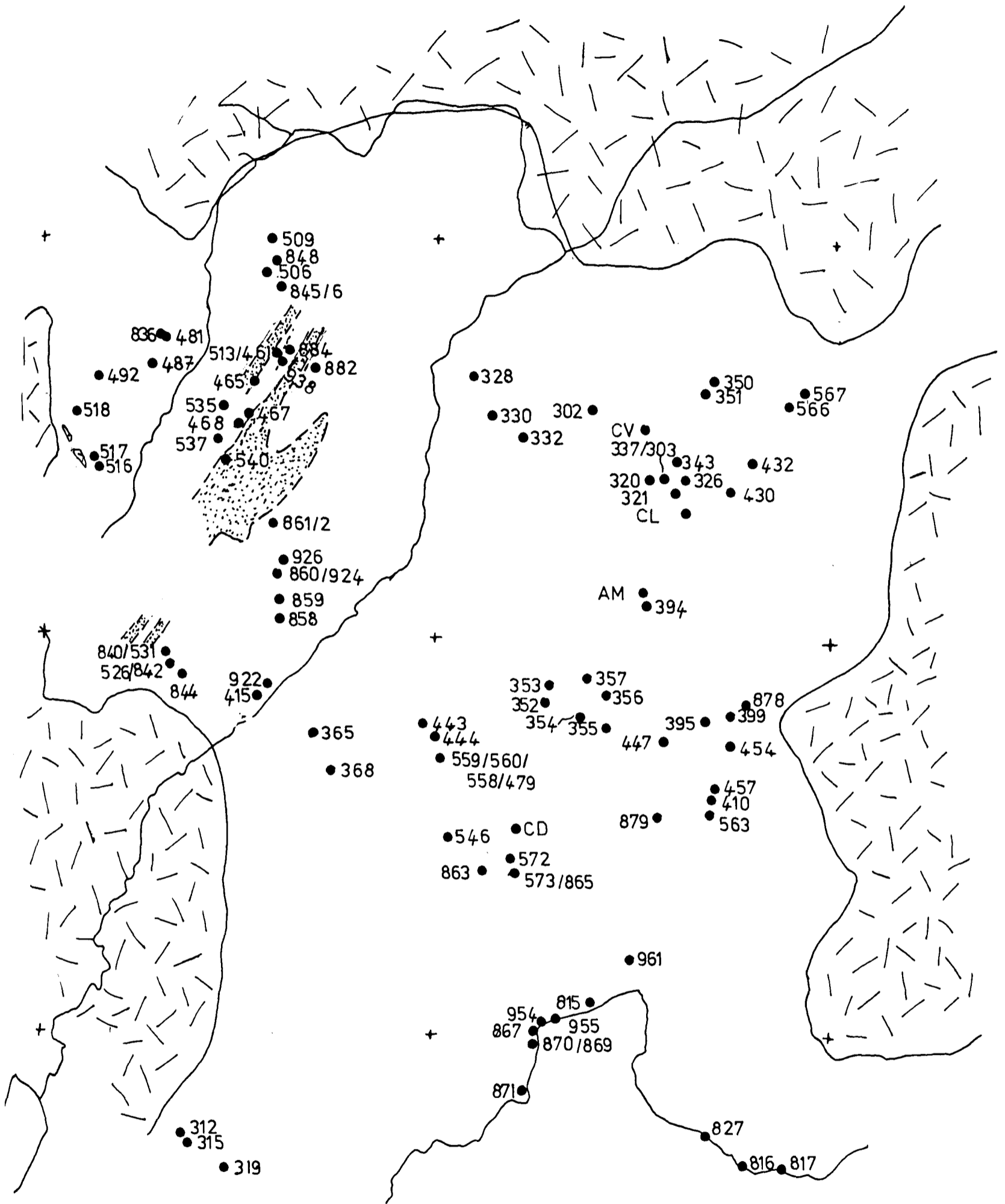
Garnet-biotite-sillimanite-muscovite-staurolite-plagioclase-quartz late staurolite and muscovite (see chapters 3 & 4).

Metabasites in Glen Muick

Garnet-clinopyroxene-hornblende-plagioclase-quartz bearing metabasites occur at : 368 (N0335885), 479 (N0350886), 355 (N0372887), 312A (323836), 303 (380919), 302 (N0372924). More leucocratic metabasites with the assemblage garnet-hornblende-plagioclase-quartz-opaques-biotite occur at N0368889 (354A) and N0364892 (352). Small amounts of biotite sometimes occur in clinopyroxene bearing assemblages. A talc-tremolite rock occurs at N0349889, which presumably represents a sliver of ultrabasic rock. Epidote occurs in some assemblages, usually in clearly retrogressed gneisses such as 309 (N0319838) & 558A (N0349889) both with the assemblage:

Hornblende-plagioclase-epidote-quartz-opaques. In 965B (N0358929) zoisite occurs rimming earlier clinopyroxene in the assemblage:

Clinopyroxene-hornblende-zoisite-plagioclase-quartz-opaques. Other assemblages in this locality are coarse hornblende gneisses with hornblende-plagioclase-quartz-opaques (e.g. 330A).



Locations of thin sections studied in the Glen Muick area

APPENDIX B

MINERAL ANALYSES

ANALYTICAL TECHNIQUE

Mineral analyses were performed on a MICROSCAN 9 electron microprobe at the department of Geology and Mineralogy, Oxford. Data was analysed on line by a ZAF correction program following the procedure of Sweatman and Long (1969). Analyses were generally performed at 20kV with a specimen current of 3.67×10^{-8} A. A raster of $3 \mu\text{m} \times 3 \mu\text{m}$ was used except for some micas where a larger raster was used in order to attempt to minimise alkali loss.

The following standards and count times were used:

Element	Count Time (s)	Standard
Na	30	Jadeite
Mg	15	Periclase
Al	12	Corundum
Si	12	Wollastonite
Ca	10	Wollastonite
K	10	Orthoclase
Ti	10	Rutile
Mn	10	Fowlerite
Fe	10	Haematite
Zn, Ba & Cr	10	Metals

Representative mineral analyses are given on the microfiche, enclosed at the end of this thesis. Rocks for which analytical data have been presented are listed in the following table. The analyses, presented are not necessarily those used for calculations which may be averages of several analyses.

Analyses are presented as oxide wt. %s (numbers ending in W) and as molecular proportions recalculated to the appropriate number of oxygens (numbers ending in M). The analyses compiled on the microfiche are listed in the table below.

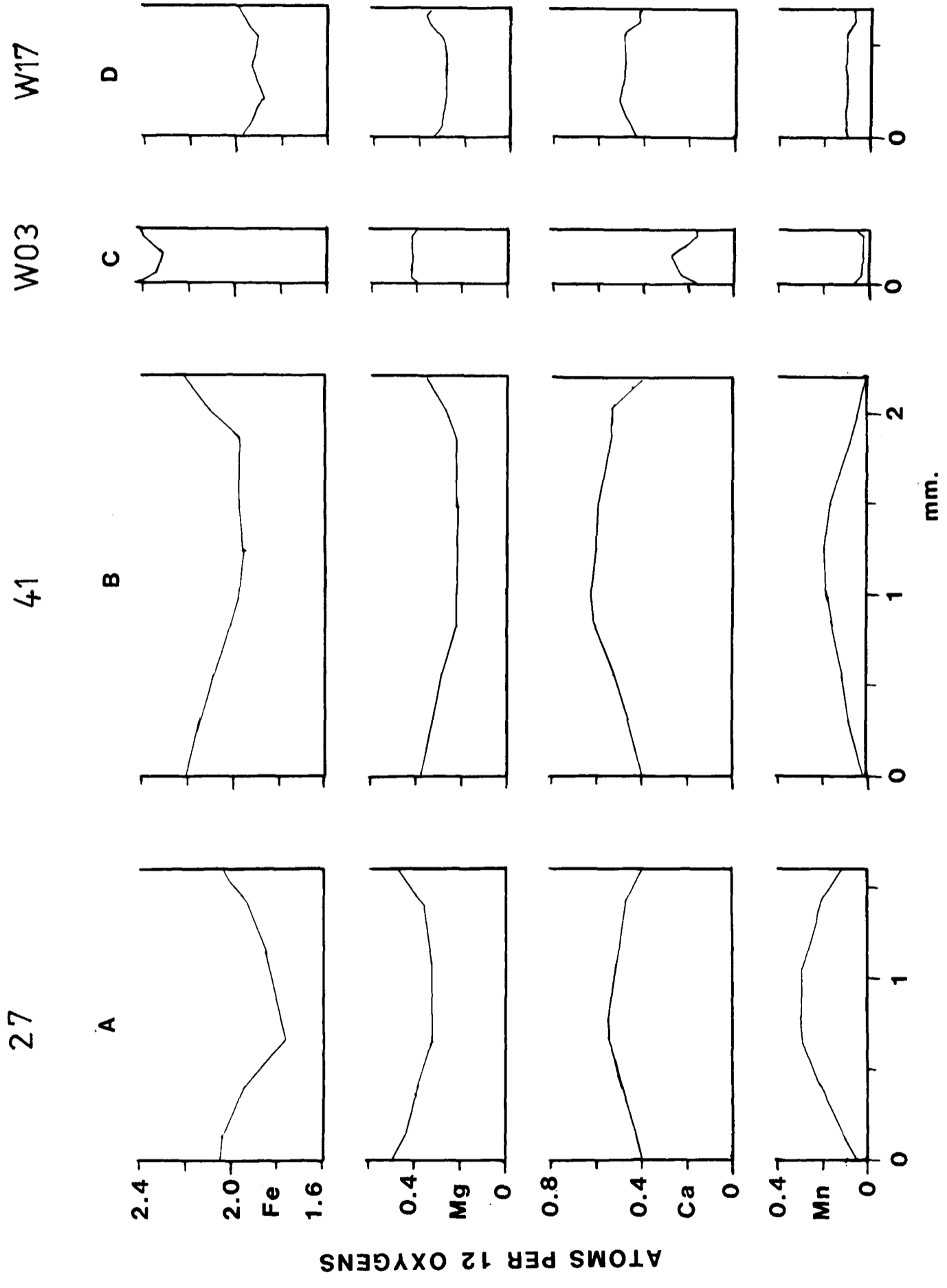
The latter part of this appendix consists of a compilation of garnet zoning profiles.

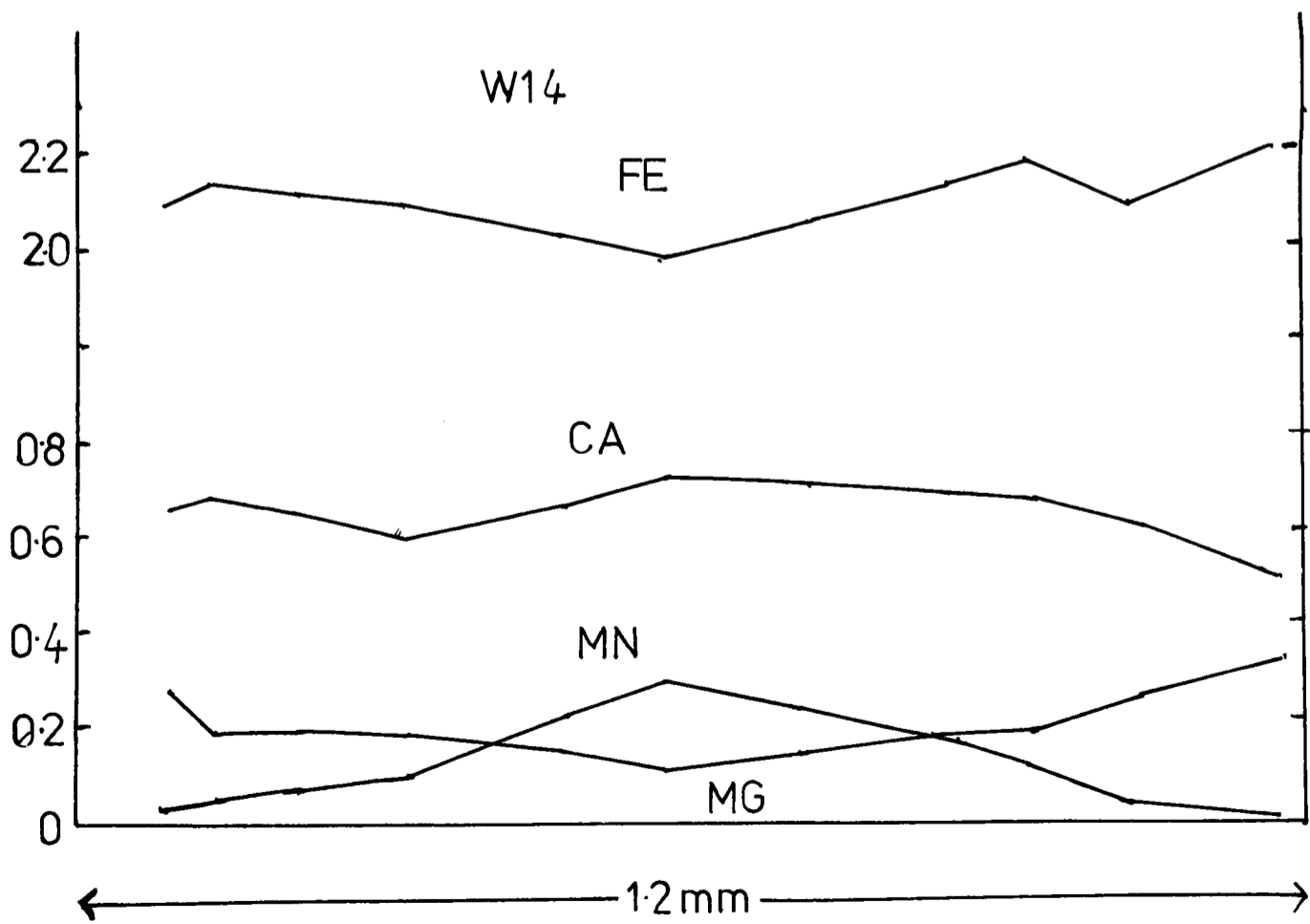
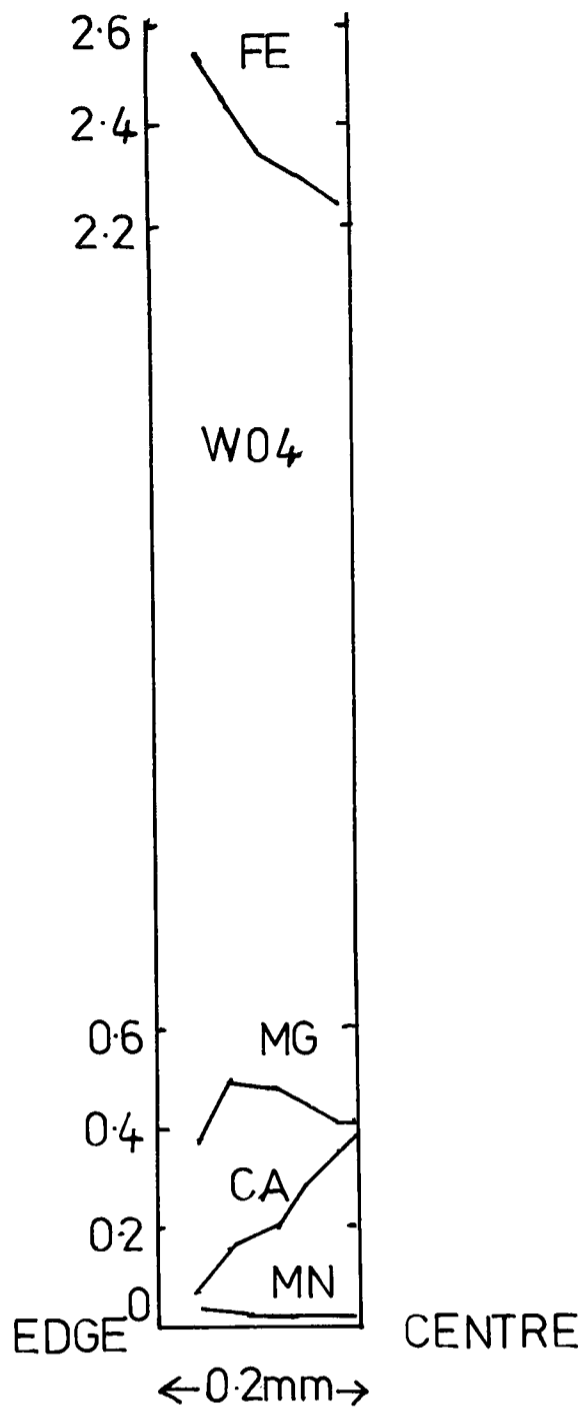
ROCK	LOCATION	ASSEMBLAGE
		(analysed minerals are underlined)
1	Glenbuchat	<u>Gt-St-Bi-Mu-Qtz-Ilm</u>
19	N of Glen Avon	<u>Gt-Bi-Chl-Mu-Qtz-Plag-St-opaques</u>
21	N of Glen Avon	<u>Gt-St-Bi-Mu-Qtz-opaques</u>
23	N of Glen Avon	<u>St-Bi-Mu-Qtz-opaques</u>
25	N of Glen Avon	<u>St-Bi-Mu-Qtz-opaques</u>
27B	Glen Avon	Ky- <u>St-Gt-Bi-Mu-Plag-Qtz-opaques-Chl</u>
37F	Glen Avon	Ky- <u>Gt-St-Bi-Mu-Plag-Qtz-Chl-opaques</u>
41A	Glen Avon	<u>Gt-Ky-St-Bi-Mu-Qtz-Plag-Parag-Chl-opaques</u>
ZZ	Glen Avon	Ky- <u>Gt-Bi-Mu-Plag-Chl-Qtz-opaques</u>
W35	Glen Avon	<u>Ky-Gt-Bi-Mu-Plag-Qtz-Chl-opaques</u>
60A	Ailnack	<u>Gt-Mu-Chl-Bi-Qtz-opaques</u>
90A	Ailnack	<u>Mu-Bi-Chl-quartz-opaques</u>
117	W of Portsoy	<u>Gt-St-Mu-Bi-Qtz-opaques</u>
GD289	Portsoy	<u>Gt-St-Mu-Bi-Qtz-opaques</u>
616A	W of Portsoy	<u>Gt-Bi-Mu-Qtz-opaques</u>
617A	W of Portsoy	<u>Gt-Bi-Mu-Qtz-opaques</u>
620B	W of Portsoy	<u>Gt-Bi-Chl-Mu-Qtz-opaques</u>
621A	W of Portsoy	<u>St-Bi-Mu-Qtz-opaques</u>
627	W of Portsoy	<u>Gt-Bi-Qtz-opaques</u>
634B	W of Portsoy	Ky- <u>St-Bi-Mu-Qtz-opaques</u>
635B	W of Portsoy	<u>St-Bi-Mu-Qtz-opaques</u>
CG2	Portsoy	<u>Gt-Bi-Plag-Qtz-fibrolite-opaq-Mu</u>
632C	Portsoy	<u>Gt-Bi-Plag-Mu-Qtz-fibrolite-opaques</u>
637B	D.H.G.	<u>Gt-Bi-Mu-Plag-Qtz-opaques</u>

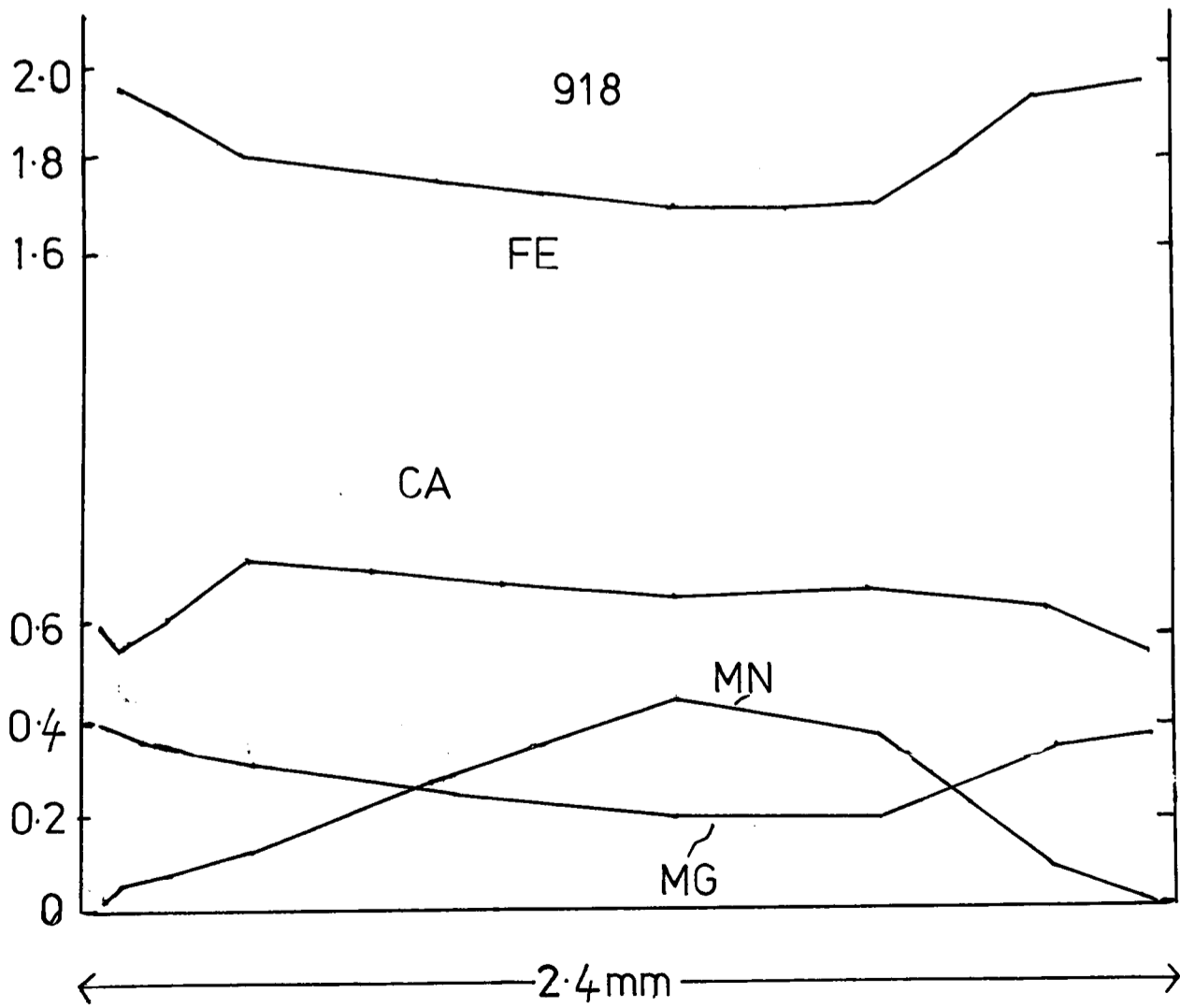
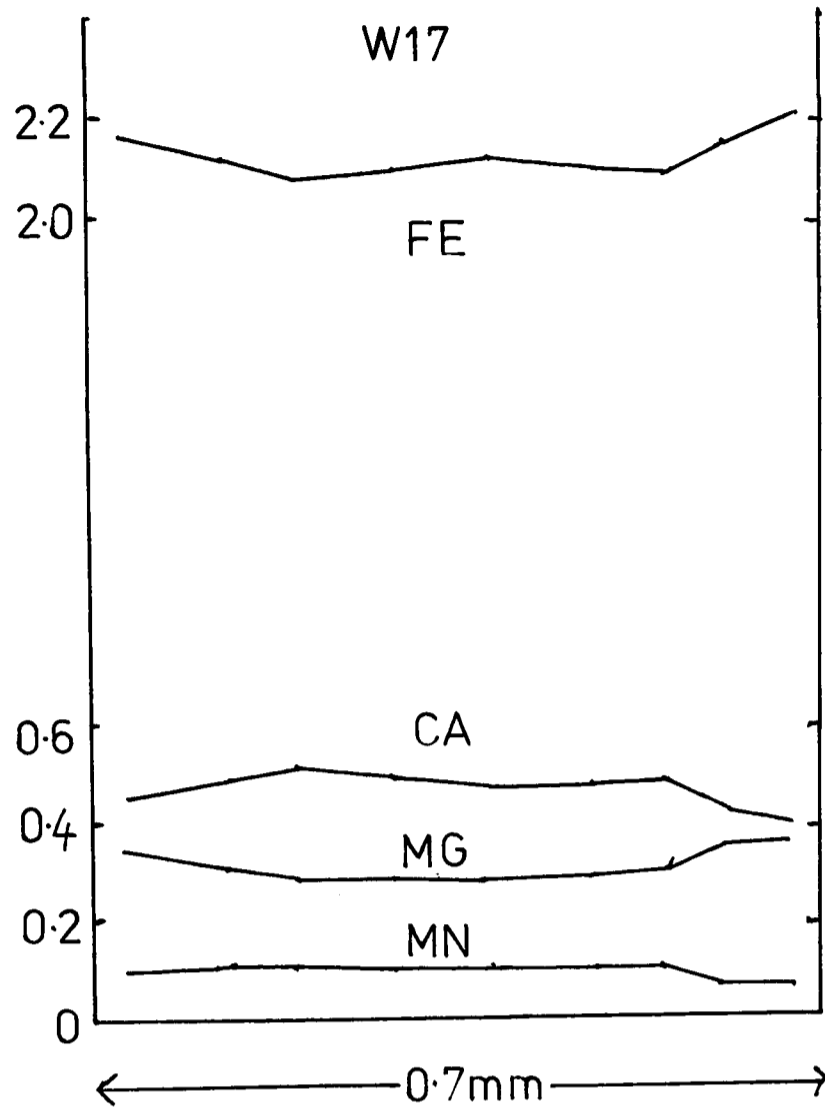
ROCK	LOCATION	ASSEMBLAGE
		(analysed minerals are underlined)
637D	D.H.G.	<u>Gt-Bi-Mu-Plag-Qtz-Ky</u> -opaques
638F	D.H.G.	<u>Gt-Bi-Mu-Plag-Qtz</u> -opaques
648A	Glen Esk	<u>Gt-St-Bi-Mu-Plag-Qtz</u> -fibrolite-opaques
648C	Glen Esk	<u>Gt-Bi-Mu-Plag-Qtz</u> -opaques
645B	Glen Esk	<u>Gt-Bi-Mu</u> -fibrolite- <u>Plag-Qtz</u> -opaques
647A	Glen Esk	<u>Gt-Bi-Mu-Plag-Qtz</u> -opaques
955A	Glen Mark	<u>Gt-Bi-Mu</u> -fibrolite- <u>Plag-Qtz</u> -opaques
956	Glen Mark	<u>Gt-Bi-Mu</u> -fibrolite- <u>Plag-Qtz-Chl</u> -opaques
155	Glen Clova	<u>Ky-Fibrolite-Gt-Bi-Mu-Plag-Qtz</u> -opaques
129A	Glen Clova	<u>Ky-Gt-Bi-Mu-Plag-Qtz</u> -opaques
135B	Glen Clova	<u>Ky-St-Gt-Bi-Mu-Plag-Qtz</u> -opaques
141A	Glen Clova	<u>Ky-Gt-Bi-Mu-Plag-Qtz</u> -opaques
155A	Glen Ey	<u>Gt-Bi-Plag-Hb</u> -opaques
178A	Glen Ey	<u>Gt-Hb-Qtz</u>
180B	Glen Ey	<u>Gt-Ky-Plag-Qtz-Mu-Bi</u> -opaques
216A	Glen Clunie	<u>Gt-Ky-Bi-Mu-Qtz</u> -opaques
W04	Schichallion	<u>Gt-Bi-Mu-Qtz-Plag-Chl</u> -opaques
W14	Glen Tilt	<u>St-Gt-Bi-Mu-Chl-Plag-Qtz</u> -opaques
W17	Schichallion	<u>Ky-St-Gt-Bi-Mu-Plag-Chl-Qtz</u> -opaques
W19	Schichallion	<u>Gt-Ky-Hb-Plag-Bi-Qtz</u> -opaques
W12	Glen Tilt	<u>Gt-Bi-Mu-Plag-Chl-Qtz</u> -opaques
W03	Schichallion	<u>Ky-Gt-Bi-Mu-Plag-Qtz</u> -opaques
CD1	Cromar	<u>Cpx-Hb-Plag-Qtz</u> -opaques
CF2	Cromar	<u>Gt-St-And-Bi-Mu-Chl-Plag-Qtz</u> -opaq.-fibrolite
566B	Glen Muick	<u>Gt-Bi-Plag-Mu-Qtz-And</u> -fibrolite-Cord-opaques

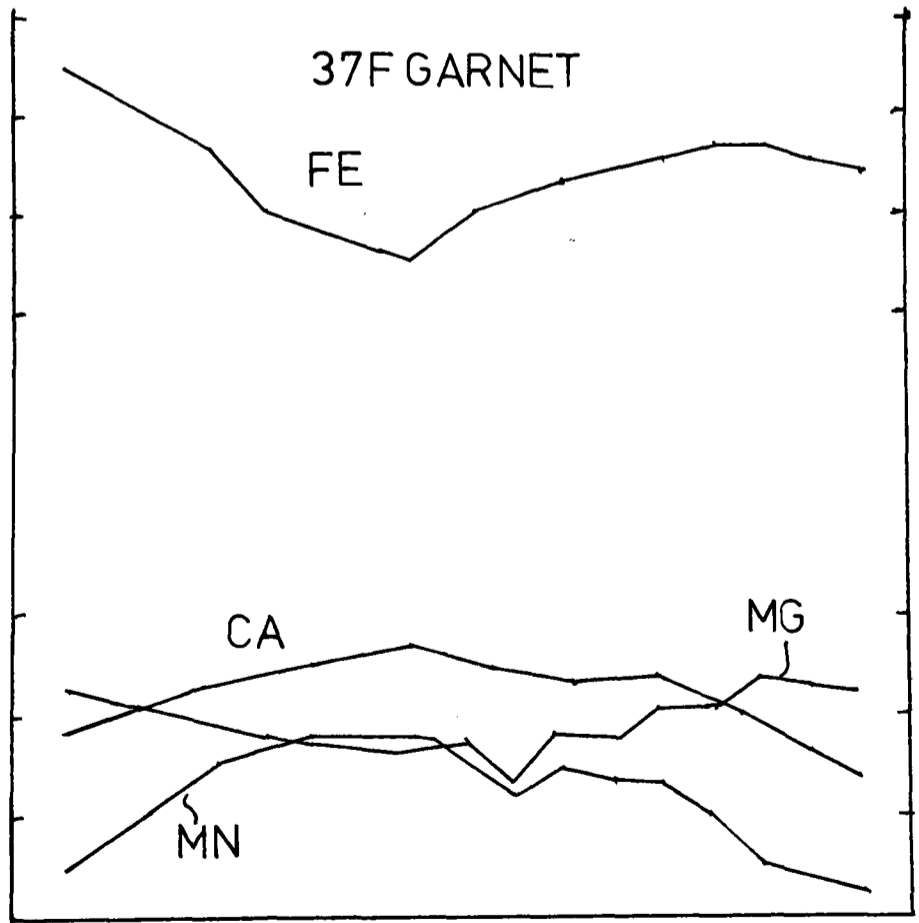
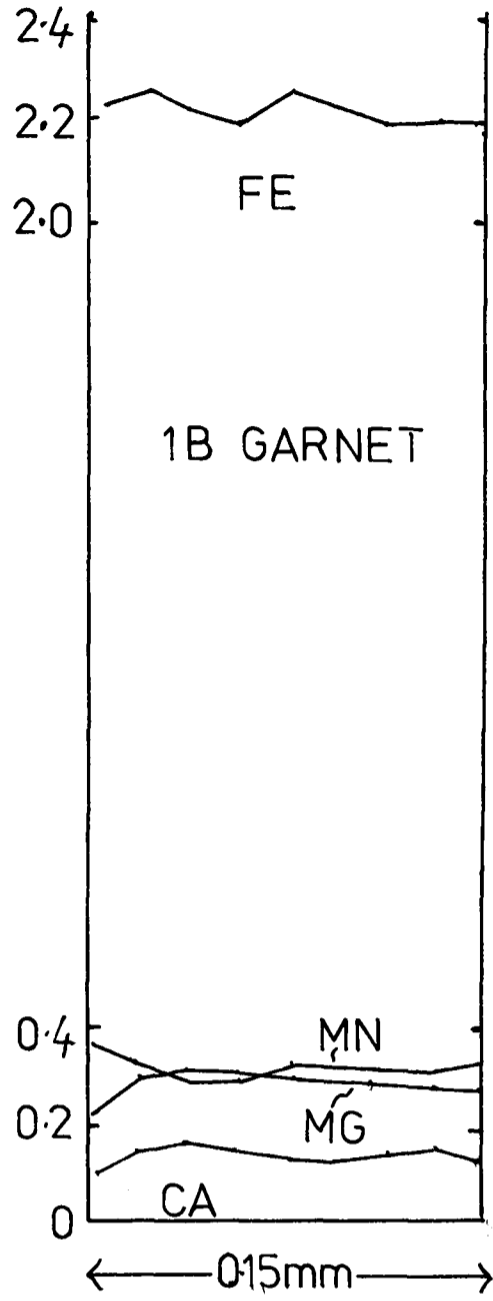
ROCK	LOCATION	ASSEMBLAGE
		(analysed minerals are underlined)
315A	Glen Muick	<u>Gt-Bi-Cumm</u> -Plag-Qtz-opaques
352	Glen Muick	<u>Hb-Bi-Plag</u> -Qtz-opaques
368	Glen Muick	<u>Gt-Cpx-Hb-Plag</u> -Qtz-opaques
430A	Glen Muick	<u>Gt-Sill-Plag-Kspar</u> -Qtz- <u>Bi</u> -opaques
595B & 595A	Cromar	<u>Gt-Sill-Plag-Bi</u> -Qtz-opaques- <u>ret. Mu</u>
919B	Cromar	<u>Gt-Sill-Plag-Kspar</u> - <u>Bi</u> -Qtz-opaques
355A	Glen Muick	<u>Gt-Cpx-Hb-Plag</u> -Qtz-opaques
540A	Glen Girnock	<u>Hb-Plag-Epid</u>
731	W of D.H.G.	<u>Gt-Mu-Bi-Parag-Plag</u> -Qtz-Chl-opaques
733	W of D.H.G.	<u>St-Gt-Bi</u> -Mu-Qtz-opaques
949C	R. Blackwater	<u>Gt-Bi-Mu-Chl</u> -Qtz-opaques
918	Glen Shee	<u>Gt-Bi-Mu-Plag</u> -Qtz-opaques
721	Glen Esk	<u>Gt-Plag-Hb</u> -Qtz-Zo-opaques
727	Glen Clova	<u>Gt-Hb-Ged-Bi-Chl-Plag</u> -Qtz-opaques
730	Glen Clova	<u>Gt-Hb-Pl</u> -Qtz-opaques
735	Glen Prosen	<u>Gt-Hb-Plag</u> -Qtz-opaques
747B	Schichallion	<u>Gt-Plag-Hb-Chl</u> -Qtz-opaques
752	Schichallion	<u>Gt-Hb-Plag</u> -Bi-Zo-Sph-Ru
801	D.H.G.	<u>Gt-Hb-Plag-Bi</u> -Qtz-opaques
807B & 809B	D.H.G.	<u>Gt-Cpx-Hb-Plag</u> -Qtz-opaques

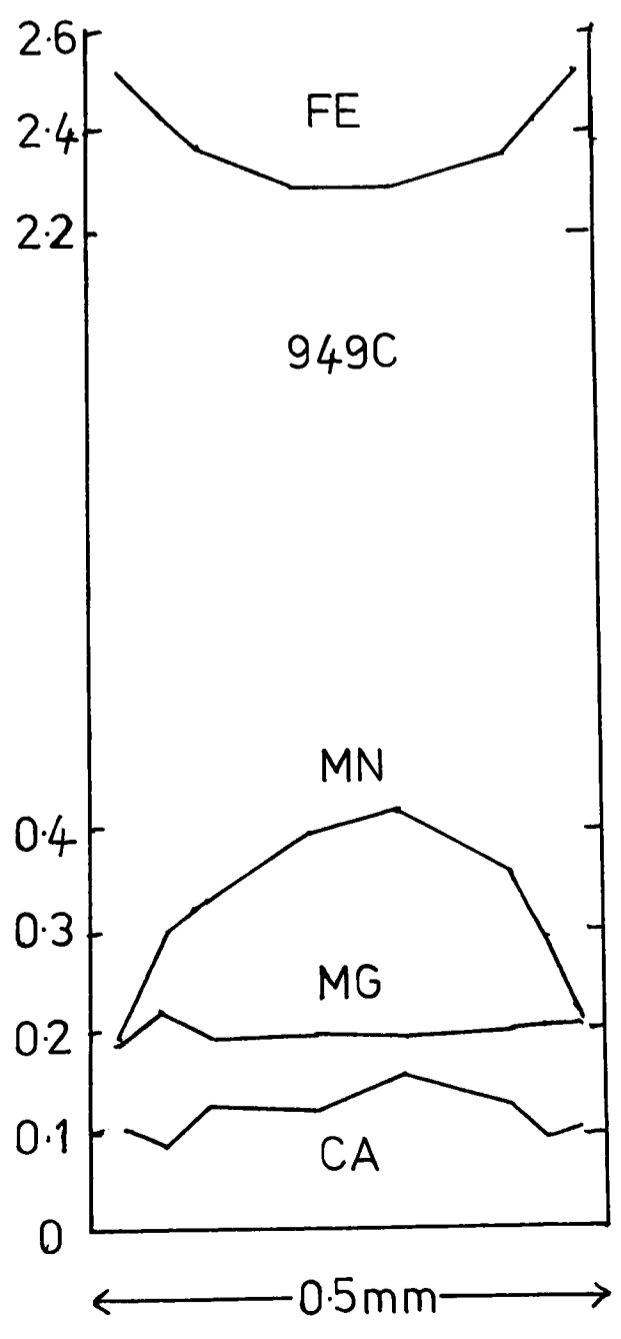
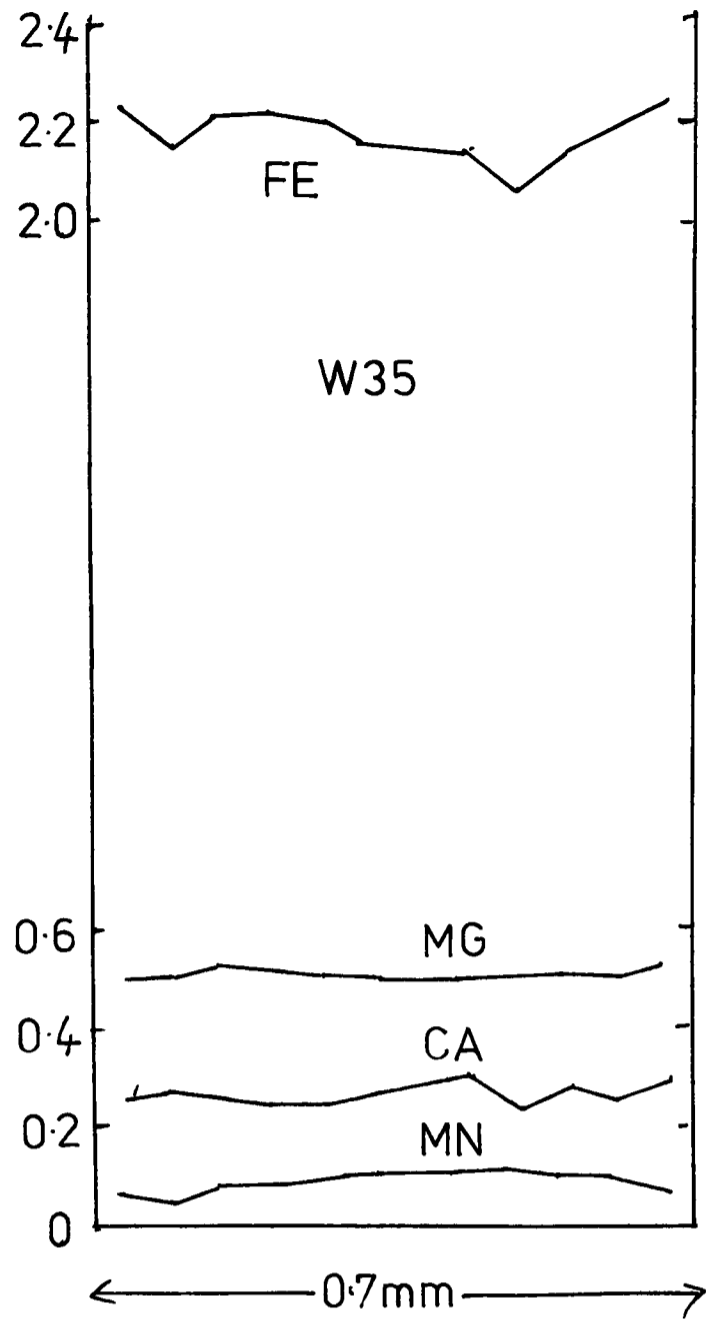
ROCK	LOCATION	ASSEMBLAGE
		(analysed minerals are underlined)
816	Glen Mark	<u>Gt-Hb-Plag-Qtz</u> -opaques
858	Glen Muick	<u>Gt-Cpx-Hb-Plag-Qtz</u> -opaques
866A	Glen Mark	<u>Gt-Hb-Plag-Qtz</u> -opaques
916C	Glen Shee	<u>Gt-Bi-Plag-Chl-Epid-Hb-Qtz</u> -opaques
606	Haddo House	<u>Gt-Cord-Plag-Bi-Opx-Qtz</u> -opaques
GM3AZ	Lochnagar	<u>Gt-Cord-Plag-Bi-Opx-Qtz</u> -opaques-
IN1	Lochnagar	And- <u>Cord-Kspar-Bi-Plag-Qtz</u> -Mu-opaques
583C	E of G. Muick	<u>Gt-Woll-Cpx-Plag-Vesuvianite</u> -opaques
MC2	Maryculter	<u>Gt-Hb-Plag-Qtz</u> -opaques-sphene
CL3	Glen Muick	<u>Gt-Cpx-Hb-Plag-Qtz</u> -opaques
CL4	Glen Muick	<u>Gt-Cpx-Hb-Plag-Qtz</u> -opaques
CL7	Glen Muick	<u>Gt-Sill-Bi-Plag-Qtz</u> -Kspar-opaques
320	Glen Muick	<u>Gt-Bi-Plag-Qtz</u> -opaques
PG2	Portsoy	<u>Gt-Bi-Plag-Amphibole-Qtz</u> -opaques

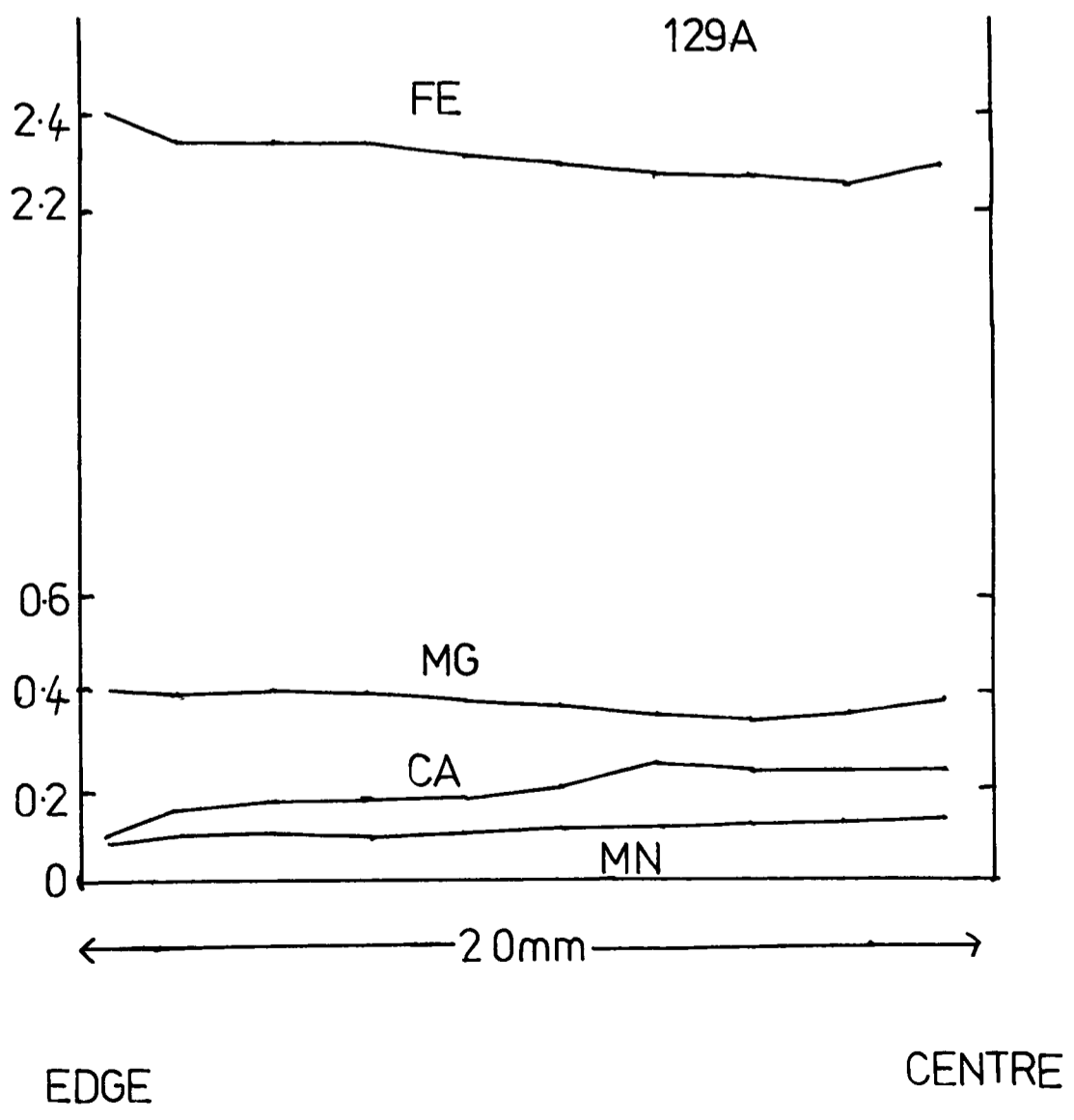
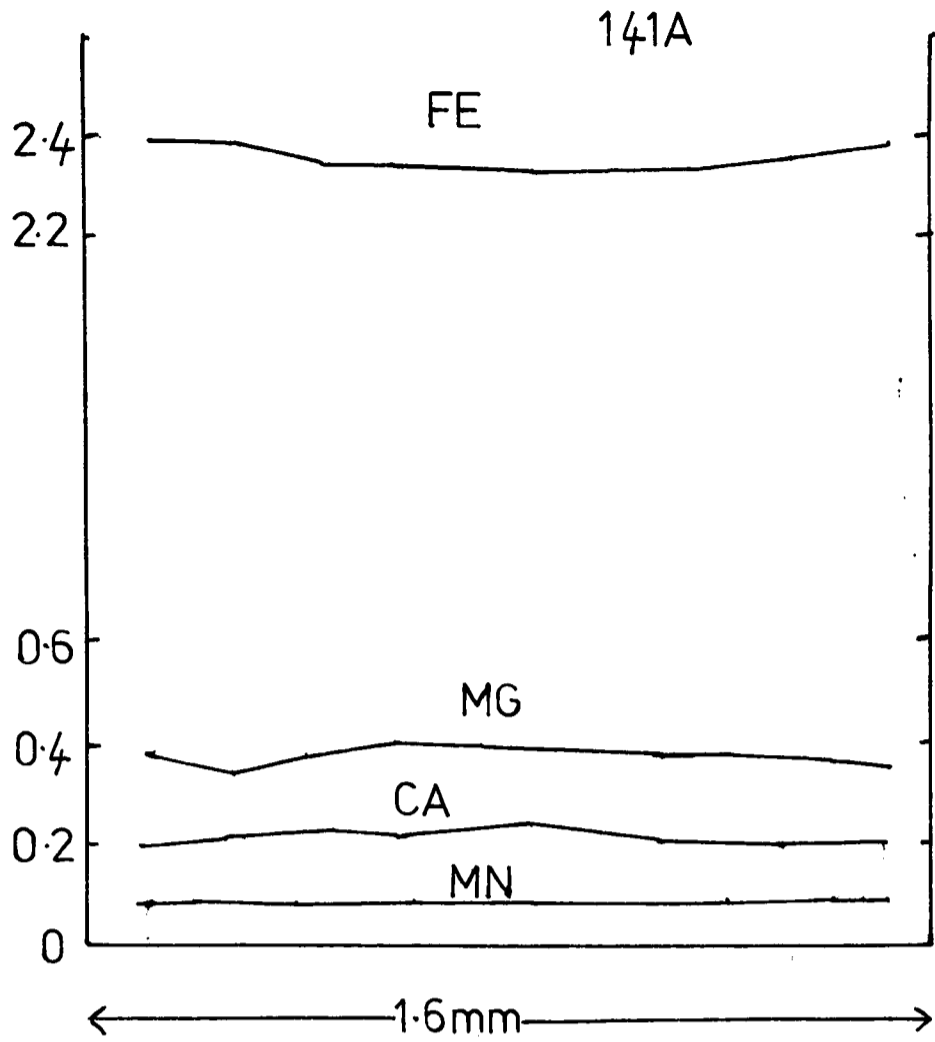


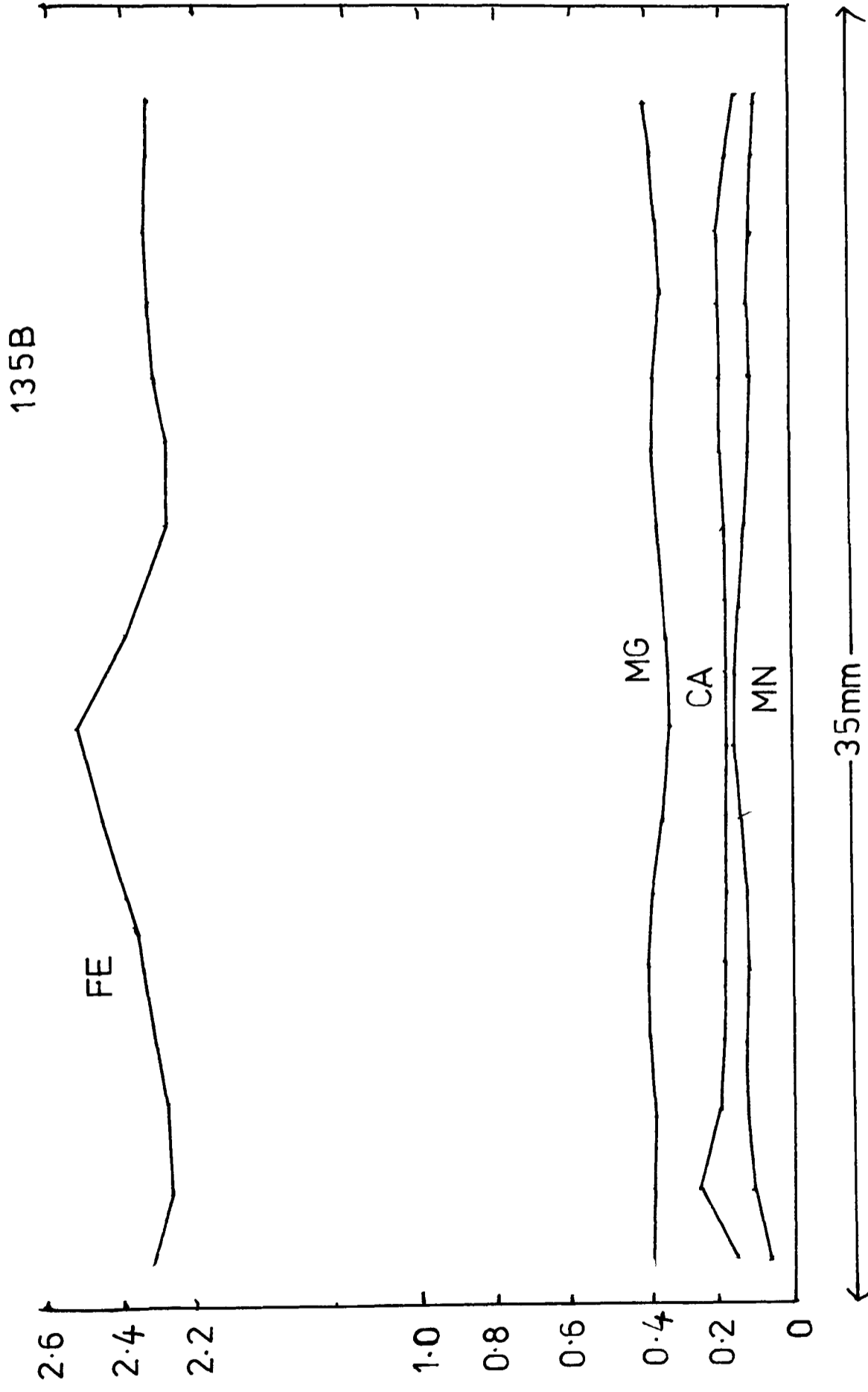


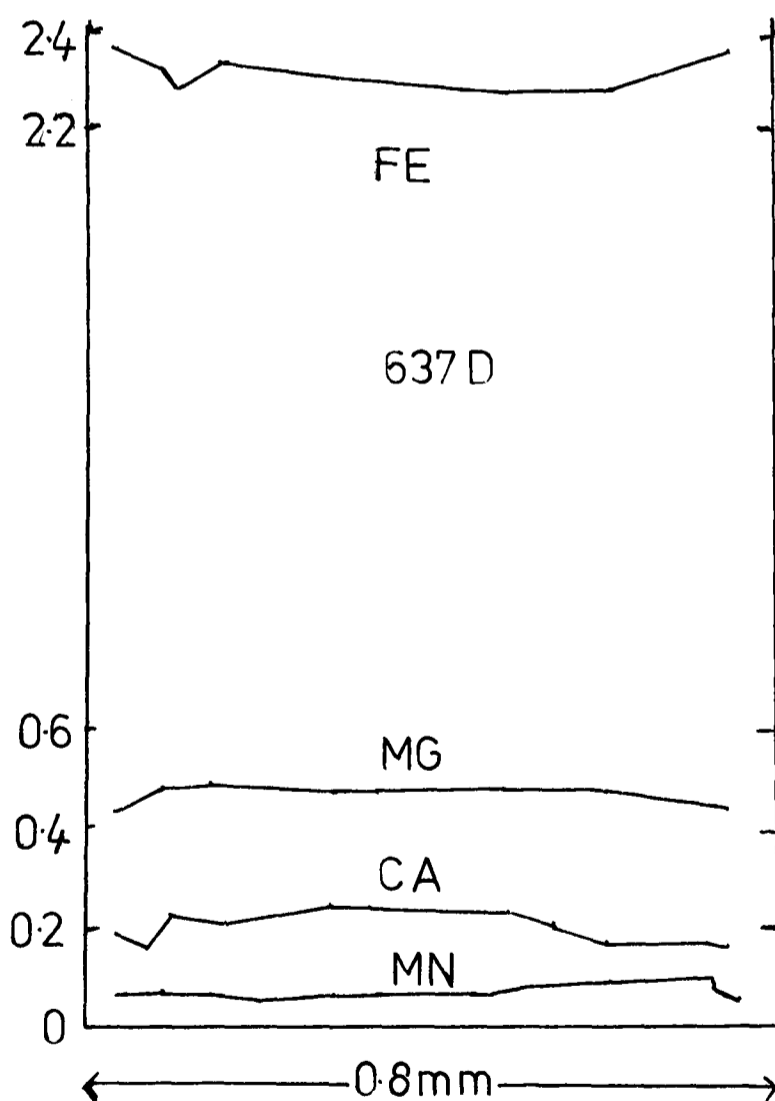
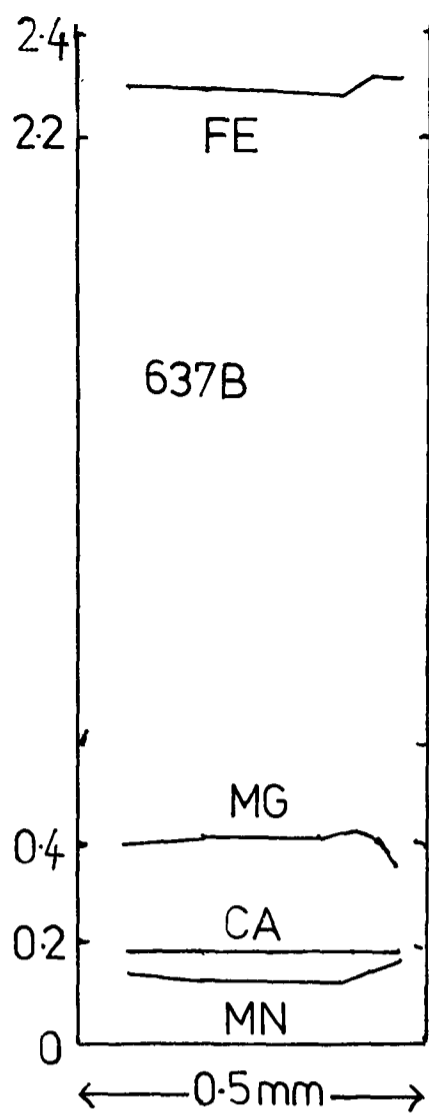


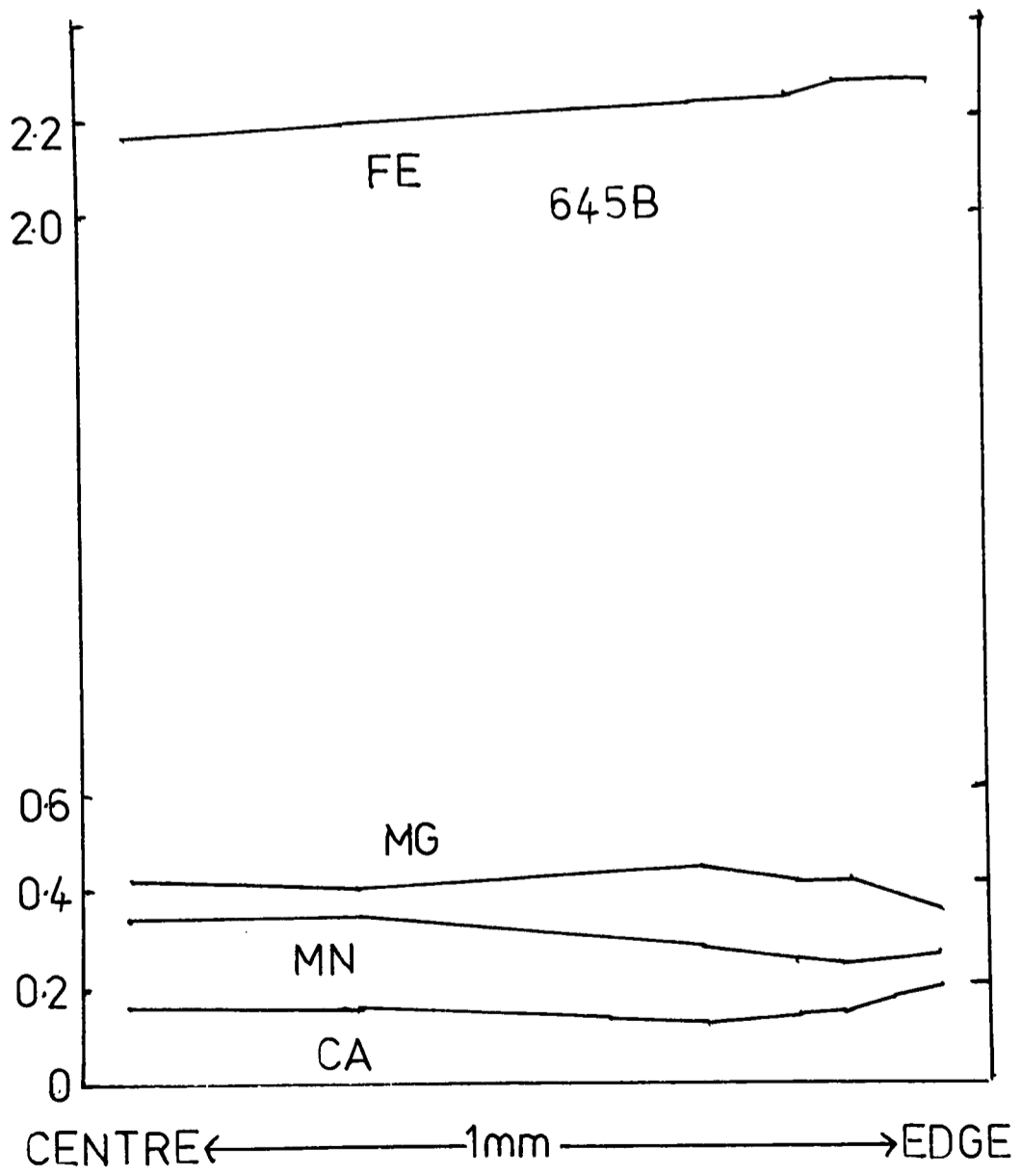
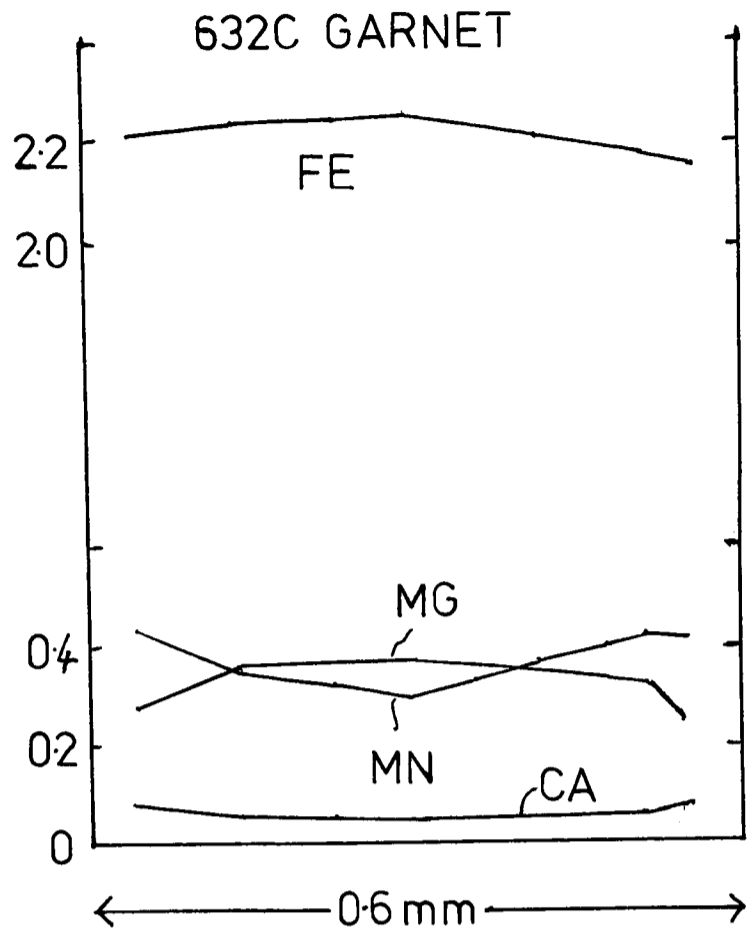


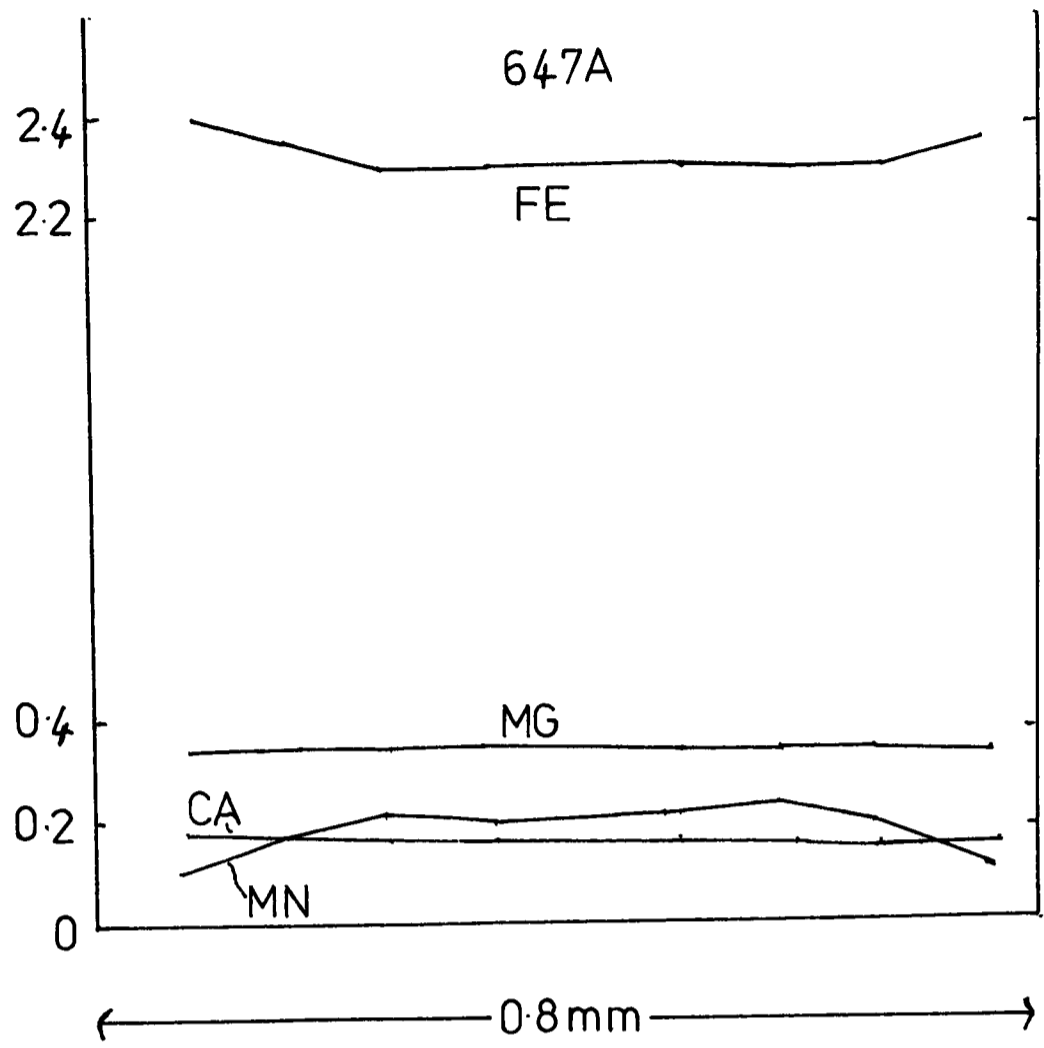


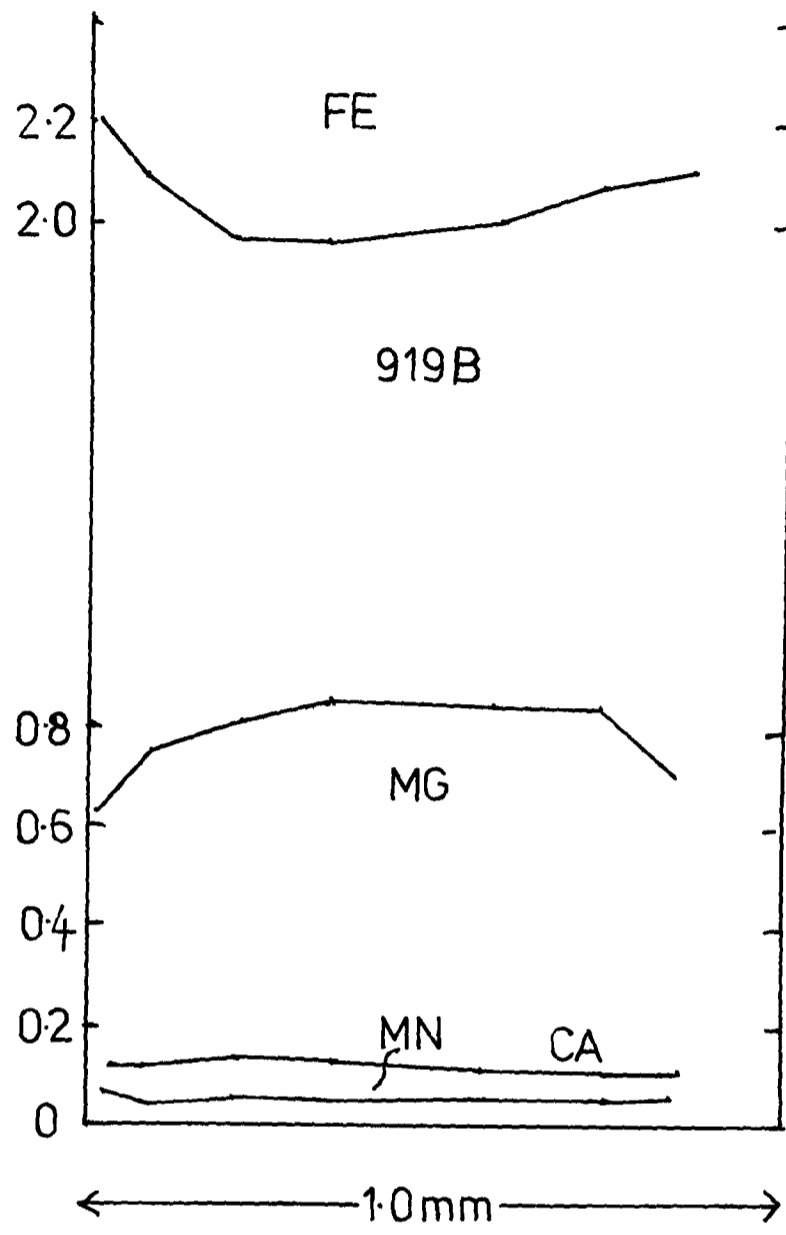


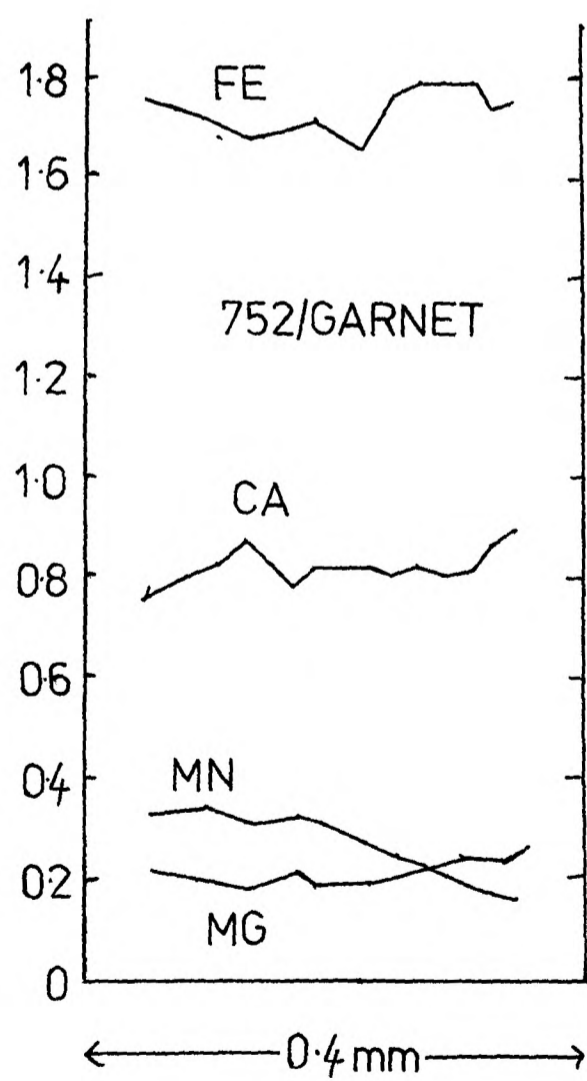
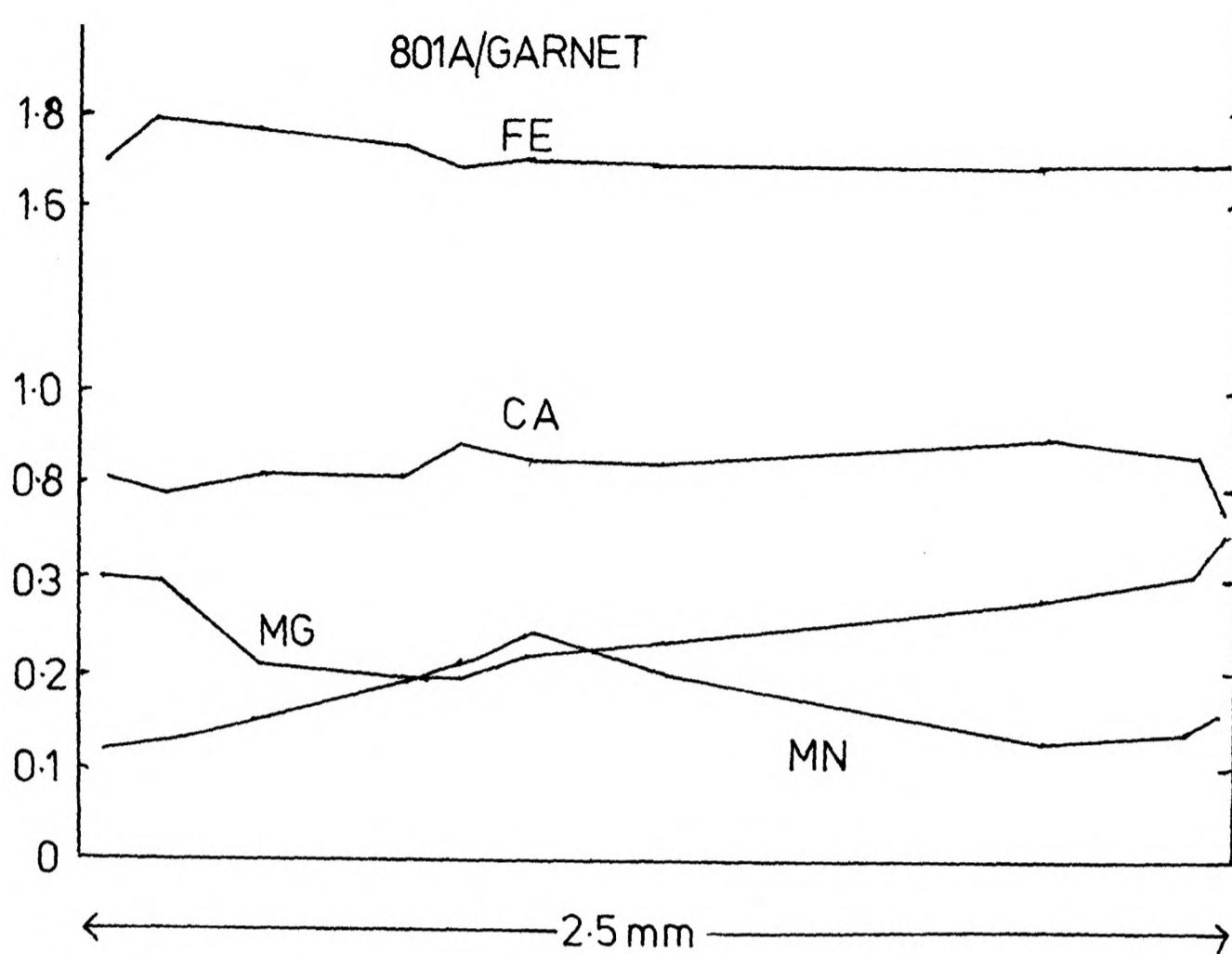


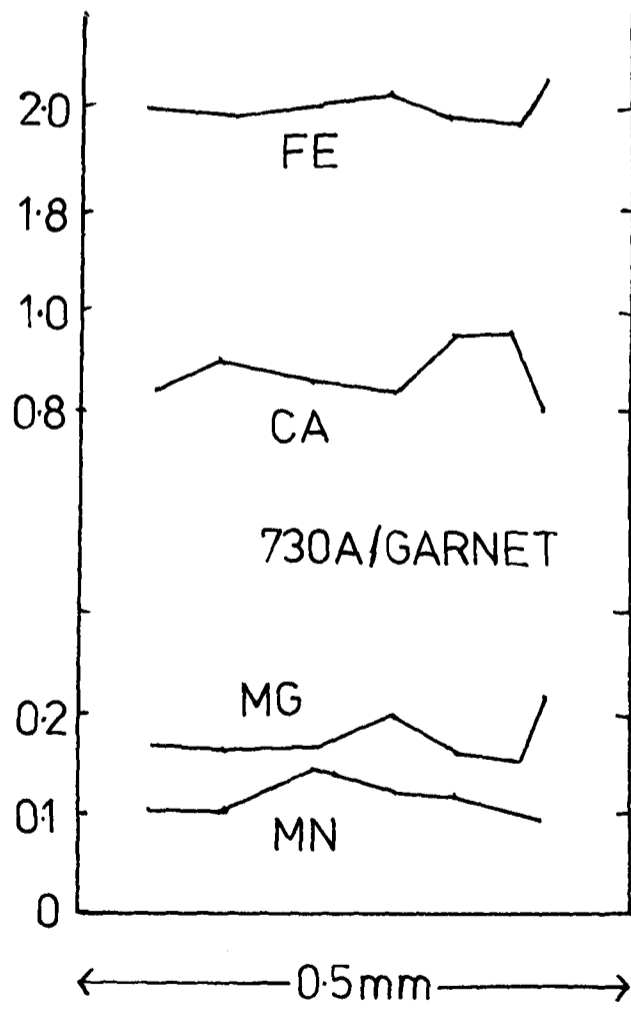
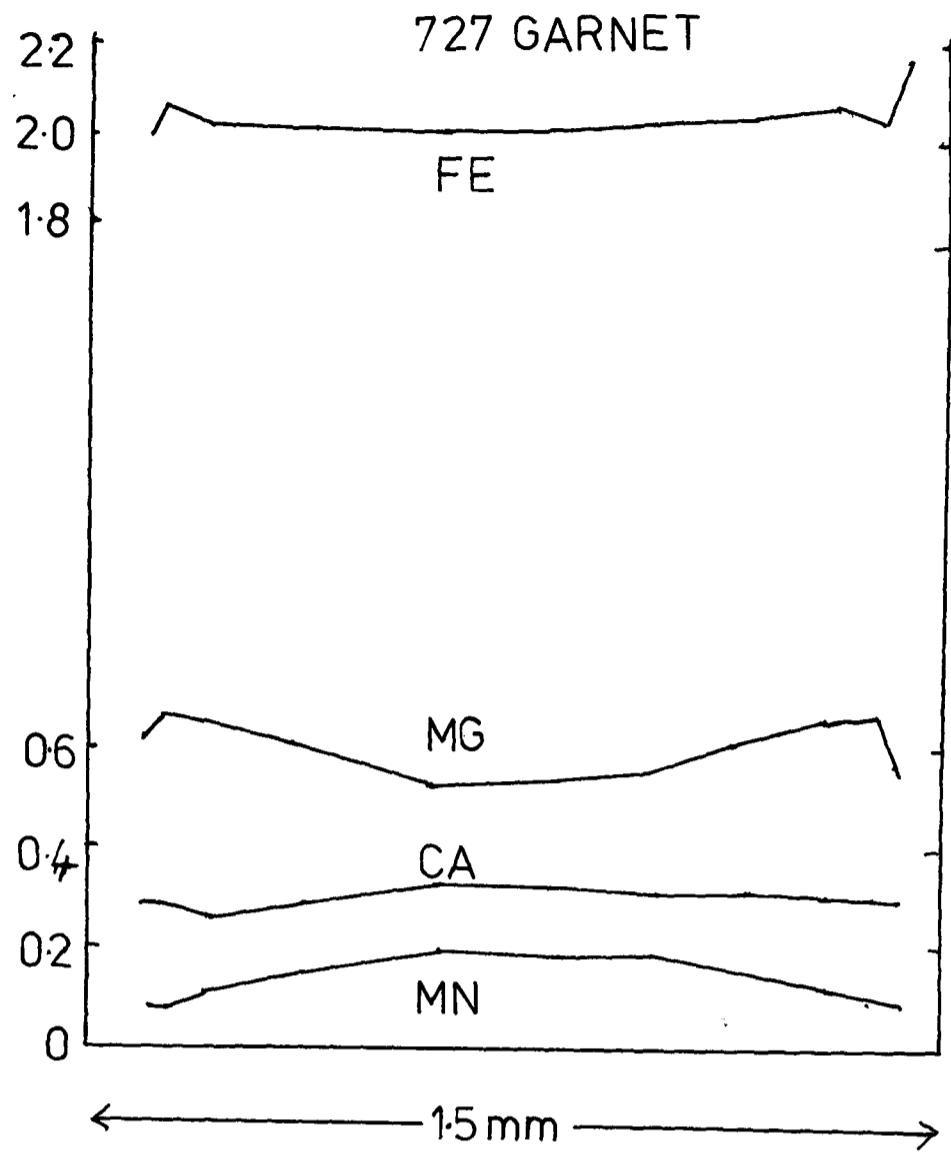


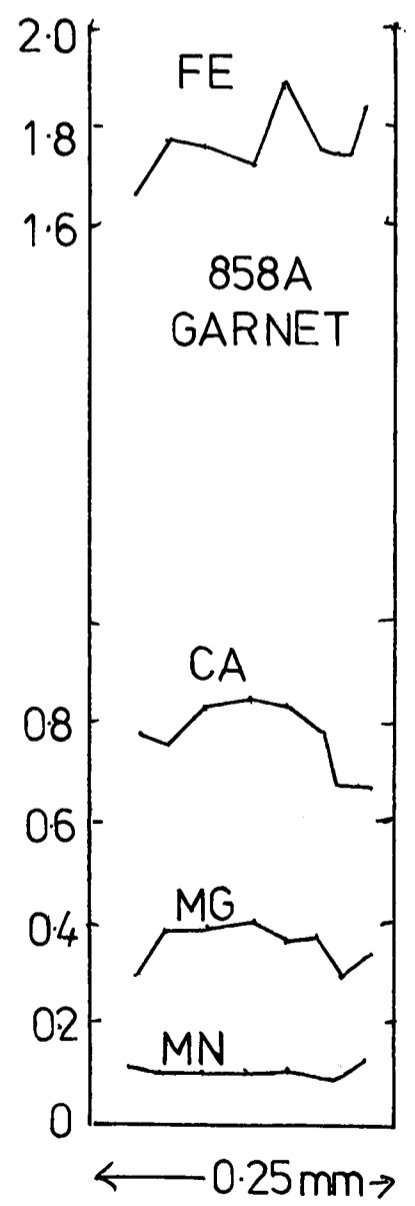
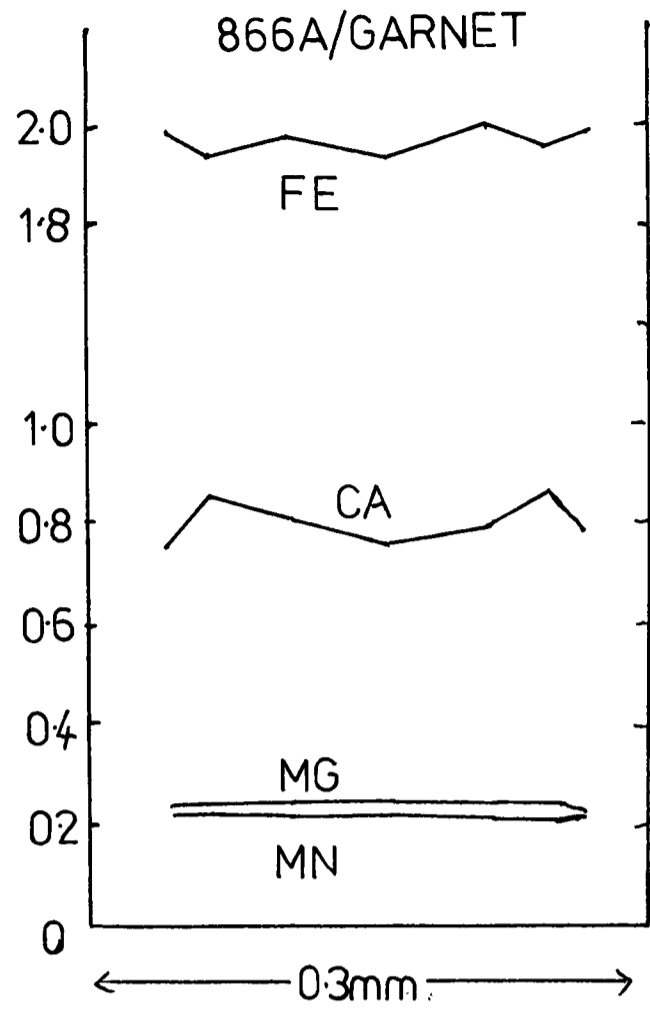












APPENDIX C

THERMODYNAMIC BACKGROUND

A brief resume of the thermodynamics employed is given in this appendix. For reviews and further information the reader is referred to Holland (1981), Saxena (1973), Helgeson et al. (1978) and Ferry and Burt (1982).

Chemical Potential

The chemical potential of a component μ_i measures the tendency of that component to migrate. At equilibrium:

$$\sum_i n_i \mu_i = 0 \quad (1)$$

where n_i are the reaction coefficients for each component i .

Gibbs Free Energy

The Gibbs free Energy of a closed system at pressure P and temperature T is defined as :

$$G = U + PV - TS \quad (2)$$

where U is the internal energy, V the volume and S the entropy.

G is given by:

$$G = \sum_i n_i \mu_i \quad (3)$$

so that at equilibrium $\Delta G = 0$ (4)

Gibbs Duhem Equation

Differentiating (3) gives :

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (5)$$

Differentiating (2) gives:

$$dG = dU + P dV + V dP - T dS - S dT \quad (6)$$

and from the first and second law of thermodynamics:

$$dU = T dS - P dV \quad (7)$$

(6) and (7) gives:

$$dG = V dP - S dT \quad (8)$$

or for a multicomponent system:

$$dG = V dP - S dT + \sum_i \mu_i dn_i \quad (9)$$

Substitution of (9) in (5) gives the Gibbs Duhem relation:

$$VdP - SdT - \sum_i n_i d\mu_i = 0 \quad (10)$$

For a system containing p phases and c components there are p Gibbs Duhem equations. The total number of intensive variables (independent of composition) is $2+c$ (P, T and $c \mu$'s). The number of independent variables is given by the total number of variables less the number of independent equations relating them i.e.:

$$F = c + 2 - p \quad (11)$$

This is the Gibbs Phase rule where F is the number of degrees of freedom of the system.

Pressure and temperature dependence of G

At P_1 and T_1 :

$$G_{P_1, T_1} = H_{P_1, T_1} - T_1 S_{P_1, T_1} \quad (12)$$

For a higher temperature T_2 :

$$G_{P_1, T_2} = G_{P_1, T_1} + \int_{T_1}^{T_2} dH - T_2 \int_{T_1}^{T_2} dS \quad (13)$$

and:

$$\frac{\partial H}{\partial T}_p = c_p \quad \text{and} \quad \frac{\partial S}{\partial T}_p = c_p / T \quad (14)$$

where c_p is the heat capacity at constant pressure.

$$G_{P_1, T_2} = G_{P_1, T_1} + \int_{T_1}^{T_2} c_p dT - T_2 \int_{T_1}^{T_2} (c_p / T) dT \quad (15)$$

Similarly :

$$G_{P_2, T_1} = G_{P_1, T_1} + \int_{P_1}^{P_2} V dP \quad (16)$$

In practice this integral is evaluated using the following equation:

$$\int_{P_1}^{P_2} \Delta V_s dP = (\Delta V_{298, P_1} + \Delta(\alpha V)(T - 298))P - \frac{1}{2} \Delta(\beta V)P^2 \quad (17)$$

where α is the coefficient of thermal expansion at 1 bar and β is the compressibility at 298K.

Fluids

An ideal fluid obeys Boyles Law :

$$PV_g = nRT \quad (18)$$

This gives :

$$\int_{P_1}^{P_2} V dP = RT \ln(P_2/P_1) \quad (19)$$

For a non ideal gas fugacity is defined:

$$fV_g = nRT \quad (20)$$

and :

$$\int_{P_1}^{P_2} V_g dP = RT \ln(f_2/f_1) \quad (21)$$

$$\text{and : } f = P \Gamma \quad (22)$$

where Γ is the fugacity coefficient.

For a reaction between solids and fluids the following relation is hence obtained:

$$G_{P_2, T_2} = G_{P_1, T_1} + \int_{T_1}^{T_2} c_p dT - T_2 \int_{T_1}^{T_2} (c_p/T) dT + \int_{P_1}^{P_2} V dP + RT \ln(f_2/f_1) \quad (23)$$

The heat capacities are often neglected for solids only reactions.

Compressibilities and expansivities may be neglected at pressures less than 10kb and temperatures less than 1000°C. For dehydration reactions for which heat capacity data does not exist heat capacities may be estimated (helgeson et al., 1978) or the approximations of Fisher and Zen (1971) or Holland (1981a) may be used.

Activity Composition Relationships

The activity of a component reflects the difference between its chemical potential at a given pressure, temperature and composition of interest and the chemical potential in some defined standard state, usually the pure phase at 298K and 1bar.

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (24)$$

standard state is chosen as 1bar and the temperature of interest:

$$\begin{aligned}\mu_i &= \mu_i^0 + \int_1^P d\mu_i \\ &= \mu_i^0 + \int_1^P V_g dP \\ &= \mu_i^0 + RT \ln f_p\end{aligned}$$

Calculation of equilibrium condition

At equilibrium $\Delta G_{p,T} = 0$.

$$\therefore 0 = \sum_{\text{products}} \mu_i n_i - \sum_{\text{reactants}} \mu_i n_i$$

At a constant pressure and temperature :

$$\begin{aligned}\Delta G_{p,T} &= \Delta G_{p,T}^0 + RT(\sum_{\text{products}} \ln a_i - \sum_{\text{reactants}} \ln a_i) \\ &= \Delta G_{p,T}^0 + RT \ln K\end{aligned}$$

$$\therefore \text{at equilibrium } \Delta G_{p,T}^0 = -RT \ln K \quad (25)$$

ΔG may be evaluated from thermodynamic data, tabulated at 1bar and various temperatures.

Ideal and non ideal mixing

The Gibbs Free Energy of a solid solution may be expressed:

$$G^{SS} = G^0 + G^M \quad (26)$$

where G^M is the Gibbs Free Energy of mixing.

$$G^0 = \sum x_i \mu_i \quad (27)$$

For an ideal solution $H^M = 0$ and $\therefore G^M = -TS^M$ (28)

A statistical treatment of the entropy of mixing gives:

$$S^M = -nR \sum_i x_i \ln x_i \quad (29)$$

$$\therefore G^{SS} = \sum_i x_i \mu_i^0 + nRT \sum_i x_i \ln x_i \quad (30)$$

Knowing that $G^{SS} = \sum_i x_i \mu_i$ and that $\sum_i x_i = 1$ it follows that :

$$\mu_i = G^{SS} + (1-x_i) \left(\frac{\partial G^{SS}}{\partial x_i} \right)_{p,T} \quad (31)$$

Differentiating 30 with respect to x_i and substituting in 31 yields:

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (32)$$

For a multisite crystalline solution:

$$a_i = x_i^n \quad (33)$$

Generalising (32) to a multiphase system at a given pressure and temperature gives the equation:

$$G_{p,T} = G_{p,T}^0 + RT \ln K \quad (34)$$

Non ideal solutions

Non ideal solutions show departure from ideality given by :

$$\mu_i = \mu_i^0 + RT \ln x_i + RT \ln \gamma_i \quad (35)$$

where γ_i is the activity coefficient and $a_i = \gamma_i x_i$ (36)

Expressing this non ideality as an excess free energy of mixing:

$$G^{XS} = G^0 + nRT \sum_i x_i \ln x_i + G^{XS} \quad (37)$$

Also $\partial G^{XS} / \partial n_i = RT \ln \gamma_i$ (38)

A number of thermodynamic models may be used to characterise non ideal solutions. Guggenheim (1937) used the following expression for a binary solution:

$$G^{XS} = x_A x_B (A_0 + A_1(x_A - x_B) + A_2(x_A - x_B)^2 + \dots) \quad (39)$$

If the A_i are all zero then the solution is ideal. If $A_0=0$, but all other A_i are zero then the solution is regular. If $A_i=0$, except for A_0 and A_1 then the solution is subregular. For a subregular solution:

$$G^{XS} = x_A x_B (A_0 + A_1(x_A - x_B)) \quad (40)$$

We know that $G^{XS} = RT \sum_i x_i \ln \gamma_i$ (41)

Differentiating with respect to x_A for a binary (A-B) solution gives the

equation:
$$RT \ln \gamma_A = x_B \frac{\partial G^{XS}}{\partial x_A} + G^{XS} \quad (42)$$

Therefore for a binary A-B subregular solution:

$$RT \ln \gamma_A = x_B^2 (A_0 + A_1(3x_A - x_B)) \quad (43)$$

This is equivalent to the Margules formulation used by Thompson (1967)

where :

$$A_0 = W_{G_1} + W_{G_2} \quad \text{and} \quad A_1 = (W_{G_1} - W_{G_2})/2 \quad (\text{Saxena, 1973})$$

$$\text{Then} \quad RT \ln \gamma_A = x_B^2 (W_{G_1} + 2x_A (W_{G_2} - W_{G_1})) \quad (44)$$

Mixing of fluids

For ideal mixing of real fluids the fugacity of a particular species is given by :

$$f_i = \Gamma_i^0 P x_i \quad (45)$$

For non ideal mixing of real fluids:

$$f_i = \gamma_i \Gamma_i^0 P x_i \quad (46)$$

The Redlich Kwong equation of state may be used to model the non ideal mixing of fluids (see Jacobs and Kerrick, 1981b). Pressures are given by :

$$P = \frac{RT}{(V-b)} - \frac{2a}{(V+bV)\sqrt{T}} \quad (47)$$

where a and b are constants, depending on the species and the temperature.

Fugacities may be extracted from:

$$\int_1^P V_i^0 dP = RT \ln (f_i^0)^{P,T} \quad (48)$$

In this study fugacities have been calculated from the modified hard sphere Redlich Kwong equation of state (Jacobs and Kerrick, 1981a).

APPENDIX D

COMPUTER PROGRAMS

PROGRAM TO CALCULATE EQUILIBRIUM TEMPERATURE OF MIXED VOLATILE REACTIONS

This calculates the equilibrium temperature of a mixed devolatilisation reaction, given input pressure and fluid composition from 1bar to 10kb and up to 1000°C. Sample input and output are listed. A further file is input to channel four and contains thermodynamic data for phases of interest. The subroutine FUGACITY is modified from the program of Jacobs and Kerrick (1981a). This calculates fugacities of H₂O and CO₂ in H₂O-CO₂ mixtures, using the MHSRK equation of Kerrick and Jacobs (1981). Temperatures are recalculated until they differ by less than one degree centigrade from the previous iteration. The program also takes account of the alpha-beta quartz transition.

```

      IMPLICIT REAL*8(A-H,P,R-Z)
      DIMENSION JCR(27),AV(27),AS(27),AH(27),AA(27),AB(27),AC(27),AD(27
1,AE(27),JA(23)
C     PROGRAM TO CALCULATE THE EQUILIBRIUM TEMPERATURE OF A GIVEN
C     MIXED VOLATILE REACTION (H2O AND CO2) AT A GIVEN PRESSURE
C     AND FLUID COMPOSITION. UTILISES THE MHSRK EQUATION OF JACOBS
C     KERRICK (1981). THE SUBROUTINE FUGACITY IS MODIFIED FROM
C     THE PROGRAM OF JACOBS AND KERRICK.
C     READS THERMODYNAMIC DATA FOR PHASE II: AV VOLUME, AS ENTROPY,
C     AH ENTHALPY AND AA TO AE HEAT CAPACITY FUNCTION COEFFICIENTS
      DO 140 II=1,26
      READ(4,10)AS(II),AH(II),AV(II),AA(II),AB(II)
      READ(4,7)AC(II),AD(II),AE(II)
140  CONTINUE
      50 READ(5,9)NQ
150  J=0
C     NQ: NO OF PHASES IN REACTION, READS PHASE NO. JA AND REACTION
C     COEFFICIENT FOR PHASE I
      DO 200 I=1,NQ
      READ(5,11)JA(I),JCR(I)
200  CONTINUE
      READ(5,9)IB
      READ(5,11)ICC,ICH
      READ(5,6)HP,ACT
      WRITE(6,16)
202  READ(5,12)PK,TC,XC,IA
C     VARIABLES ARE:
C     IB EQUALS 0 OR 1 DEPENDING ON HOW ENTHALPY OF REACTION IS INPUT

```

```

C      ICC AND ICH REACTION COEFFS OF CO2 AND H2O
C      HP ENTHALPY OF REACTION AT 1,298
C      ACT EQUILIBRIUM CONSTANT
C      PK PRESSURE KB
C      TC TEMP DEG CENTIGRADE
C      XC PROPORTION OF CO2 IN THE FLUID
C      EQUALS 0 IF CONTINUING WITH SAME REACTION, 1 FOR NEW REACTION
C      HH ENTHALPY 1,298 (CALCULATED)\
C      HMM HEAT CAPACITY INTEGRAL FOR HH AT T OF INTEREST
C      SS ENTROPY 298
C      SNN HEAT CAPACITY INTEGRAL FOR SS AT T OF INTEREST
C      VV VOLUME
C      Z, W, Y: RLNK FOR K, F(H2O) AND F(CO2)
C      T=TC+273.1500
C      XH=1.000-XC
C      PK=PK*1000.000
203   PK=PK/1000.000
C      TC=T-273.1500
C      SUBROUTINE RETURNS VALUES OF FUGACITY OF CO2 FCCM, AND OF H2O
C      FCWM:
C      CALL FUGACITY(PK,TC,XC,FCCM,FCWM)
C      PK=PK*1000.000
C      FY=FCWM*XH*PK
C      FZ=FCCM*XC*PK
C      IF(ACT.LT.0.0000100) GO TO 204
C      W=8.31400*T*(DLOG(ACT))
204   IF(FY.LT.0.000100) GO TO 206
C      Z=FLOAT(ICH)*8.31400*T*(DLOG(FY))
206   IF(FZ.LT.0.000100) GO TO 207
C      Y=FLOAT(ICC)*8.31400*T*(DLOG(FZ))
207   CONTINUE
C      DO 205 L=1,NQ
C      IG=JA(L)
C      JCS=JCR(L)
C      VV=VV+(FLOAT(JCS)*AV(IG))
205   CONTINUE
C      DO 210 K=1,NQ
C      IG=JA(K)
C      JCS=JCR(K)
C      SS=SS+(FLOAT(JCS)*AS(IG))
210   CONTINUE
C      IF(IB.EQ.1) GO TO 216
C      DO 215 M=1,NQ
C      IG=JA(M)
C      JCS=JCR(M)
C      HH=HH+(FLOAT(JCS)*AH(IG))
215   CONTINUE
C      GO TO 218
216   HH=HP
218   CONTINUE
C      DO 220 Q=1,NQ
C      IG=JA(Q)
C      JCS=JCR(Q)
C      A=AA(IG)
C      B=AB(IG)
C      C=AC(IG)
C      D=AD(IG)
C      E=AE(IG)
C      FOLLOWING SECTION INCORPORATES THE ALPHA BETA QUARTZ TRANSITION
C      IF(IG.EQ.1) GO TO 393
C      GO TO 400

```

```

393 IF(T.LT.844.000) GO TO 400
    A=58.92800
    B=0.01003100
    C=0
    D=0
    E=0
400 HM=(A*T)+(B*T*T/2)
    SN=(A*DLOG(T))+(B*T)
    HM=HM+((C/3)*T*T*T)
    SN=SN+(C*T*T/2)
    HM=HM+(2*D*(T**0.5000))
    SN=SN-(2*D*(T**-0.5000))
    HM=HM-(E/T)
    SN=SN-(E/(2*T*T))
    IF(J.EQ.1) GO TO 442
    SNN=SNN+(FLOAT(JCS)*SN)
    HMM=HMM+(FLOAT(JCS)*HM)
    GO TO 450
442 HMM=HMM-(FLOAT(JCS)*HM)
    SNN=SNN-(FLOAT(JCS)*SN)
    GO TO 467
450 QR=T
    IF(IG.EQ.1) GO TO 453
    GO TO 460
453 IF(T.LT.844.000) GO TO 460
    T=844.000
    HMM=HMM+(FLOAT(JCS)*3441800)
    SNN=SNN+(FLOAT(JCS)*62.6500)
    GO TO 465
460 T=298.1500
465 J=1
    GO TO 400
467 J=0
    T=QR
220 CONTINUE
    TN=((VV*PK)+Z+W+Y+HH+HMM)/(SNN+SS)
    TZ=TN-T
    T=TN
    IF(TZ.GT.150.000) GO TO 1000
    IF(TZ.LT.-150.000) GO TO 1000
    IF(TZ.LT.1.000) GO TO 470
    HMM=0.0
    SNN=0.0
    SS=0.0
    VV=0.0
    W=0.0
    Y=0.0
    Z=0.0
    GO TO 203
470 IF(TZ.GT.-1.000) GO TO 480
    HMM=0.0
    SNN=0.0
    SS=0.0
    VV=0.0
    W=0.0
    Y=0.0
    Z=0.0
    GO TO 203
480 CONTINUE
    WRITE(6,17)HH,SS,PK,T,XC
    IF(TK.GT.1250.000) GO TO 1000

```

```

HMM=0.0
VV=0.0
Z=0.0
W=0.0
Y=0.0
SS=0.0
SNN=0.0
IF(IA.EQ.1) GO TO 50
GO TO 202
6 FORMAT(F8.0,F5.3)
9 FORMAT(I3)
7 FORMAT(F12.10,F12.2,F12.0)
10 FORMAT(F12.2,F12.1,F12.4,F12.3,F12.8)
11 FORMAT(2I4)
12 FORMAT(F7.0,1X,F7.0,1X,F5.0,1X,I3)
16 FORMAT('0',15X,'H',15X,'S',10X,'P',15X,'T',9X,'XC02')
17 FORMAT('0',10X,F9.0,3X,F7.2,8X,F6.1,8X,F6.1,8X,F5.3)
1000 CONTINUE
STOP
END
SUBROUTINE FUGACITY(PK,TC,XC,FCCM,FCWM)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
COMMON /MNRVAR/P,T,R,T12
50 R=83.1400
BW=29.0000
BC=58.0000
XW=1.000-XC
P=PK*1000.000
T=TC+273.1500
T15=DSQRT(T**3)
T12=DSQRT(T)
RT=R*T15
CC=(28.3100+0.1072100*T-0.0000088100*T*T)*1000000.000
DC=(9380.000-8.5300*T+0.00118900*T*T)*1000000.000
EC=(-368654.000+715.900*T+0.153400*T*T)*1000000.000
CW=(290.7800-0.3027600*T+0.0001477400*T*T)*1000000.000
DW=(-8374.000+19.43700*T-0.00814800*T*T)*1000000.000
EW=(76600.000-133.900*T+0.107100*T*T)*1000000.000
IF(TC.GT.1050.000) GO TO 299
BM=(BC*XC)+(BW*XW)
CIJ=DSQRT(CC*CW)
DIJ=DSQRT(DC*DW)
EIJ=DSQRT(EC*EW)
CM=(CC*XC*XC)+(CW*XW*XW)+(2.000*XC*XW*CIJ)
DM=(DC*XC*XC)+(DW*XW*XW)+(2.000*XC*XW*DIJ)
EM=(EC*XC*XC)+(EW*XW*XW)+(2.000*XC*XW*EIJ)
299 DO 300 J=1,2
CALL ZPURE(PK,ZC,VC,ZW,VW,TC)
300 CONTINUE
IF(TC.GT.1050.000) GO TO 499
CALL ZMIX(XC,XW,VM,ZM,VC,VW,BM,CM,DM,EM)
499 DO 500 L=1,2
CALL FPURE(P,RT,FKWP,FKCP,FWP,FCP,ZC,VC,ZW,VW)
500 CONTINUE
IF(TC.GT.1050.000) GO TO 700
DO 700 M=1,2
CALL FMIX(P,RT,CIJ,DIJ,EIJ,XC,XW,BM,FCCM,FCWM,FCM,FWM,VM,ZM,CM,DM,
1EM)
700 CONTINUE
RETURN

```

```

END
SUBROUTINE ZPURE(PK,ZC,VC,ZW,VW,TC)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
IF(J.NE.1) GO TO 210
B=BC
C=CC
D=DC
E=EC
IF(PK.GE.1.000) VI=35.00
IF(PK.GE.0.1000 .AND. PK.LT.1.000) VI=100.00
IF(PK.GE.0.00500 .AND. PK.LT.0.1000) VI=500.00

IF(PK.LT.0.00500) VI=50000.0
GO TO 250
210 B=BW
C=CW
D=DW
E=EW
IF(PK.GE.1.000) VI=15.00
IF(PK.GE.0.6000 .AND. PK.LT.1.000) VI=22.50
IF(PK.GE.0.2100 .AND. PK.LT.0.6000 .AND. TC.GE.550.000) VI=75.00
IF(PK.GE.0.2100 .AND. PK.LT.0.6000 .AND. TC.LT.550.000) VI=35.00
IF(PK.GE.0.1000 .AND. PK.LT.0.2100 .AND. TC.LT.400.000) VI=15.00
IF(PK.GE.0.1000 .AND. PK.LT.0.2100 .AND. TC.GE.400.000) VI=100.00
IF(PK.GE.0.00500 .AND. PK.LT.0.1000) VI=500.00
IF(PK.LT.0.00500) VI=7000.00
250 CALL NEWRAP(B,C,D,E,Z,V,VI,PK)
IF(J.NE.1) GO TO 260
ZC=Z
VC=V
GO TO 299
260 ZW=Z
VW=V
299 RETURN
END
SUBROUTINE ZMIX(XC,XW,VM,ZM,VC,VW,BM,CM,DM,EM)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
VI=(VC*XC)+(VW*XW)
B=BM
C=CM
D=DM
E=EM
CALL NEWRAP(B,C,D,E,Z,V,VI,PK)
VM=V
ZM=Z
RETURN
END
SUBROUTINE NEWRAP(B,C,D,E,Z,V,VI,PK)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MNRVAR/P,T,R,T12
DO 350 K=1,50
Y=B/(4.000*VI)
X=(1.000-Y)
BI=(VI+B)
BI2=(VI+B)**2
PN=1.000+Y+(Y**2)-(Y**3)
PR=(PN/(VI*(X**3)))*R*T
PA1=C+(D/VI)+(E/(VI*VI))
PA2=PA1/(T12*VI*BI)

```

```

F=PR-PA2-P
D1=(-3.000*B)/(4.000*(VI**3)*X**4)
D2=-1.000/((VI**2)*(X**3))
D3=1.000/(VI*(X**3))
D4=-8/(4.000*VI**2)
D5=-2.000*(B**2)/(16.000*(VI**3))
D6=3.000*(B**3)/(64.000*(VI**4))
DPR=((PN*(D1+D2))+(D3*(D4+D5+D6)))*R*T
D7=(-1.000/(VI*BI2))+(-1.000/(VI**2*BI))
D8=1.000/(VI*BI)
D9=(-D/VI**2)+((-2.000*E)/(VI**3))
DPA=(PA1*D7+D8*D9)/T12
DF=DPR-DPA
V=VI-(F/DF)
DIFF=DABS(V-VI)
IF(DIFF.LT.0.01D0) GO TO 360
VI=V
350 CONTINUE
360 Z=(V*P)/(R*T)
RETURN
END
SUBROUTINE FPURE(P,RT,FKWP,FKCP,FWP,FCP,ZC,VC,ZW,VW)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
IF(L.NE.1) GO TO 450
B=BC
C=CC
D=DC
E=EC
V=VC
Z=ZC
GO TO 460
450 B=BW
C=CW
D=DW
E=EW
V=VW
Z=ZW
460 Y=B/(4.000*V)
FCP=((8.000*Y-9.000*Y*Y+3.000*Y**3)/((1.000-Y)**3))-(DLOG(Z))
FCP=FCP-(C/(RT*(V+B)))-(D/(RT*V*(V+B)))
FCP=FCP-(E/(RT*V*V*(V+B)))+(C/(RT*B))*(DLOG(V/(V+B)))
FCP=FCP-(D/(RT*B*V))+((D/(RT*B*B))*(DLOG((V+B)/V)))
FCP=FCP-(E/(RT*2.000*B*V*V))+(E/(RT*B*B*V))
FCP=FCP-((E/(RT*B**3))*(DLOG((V+B)/V)))
FCP=DEXP(FCP)
IF(L.NE.1) GO TO 470
FKCP=FCP
GO TO 499
470 FKWP=FCP
499 RETURN
END
SUBROUTINE FMIX(P,RT,CIJ,DIJ,EIJ,XC,XW,BM,FCCM,FCWM,FCM,FWM,VM,ZM,
1CM,DM,EM)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
B=BM
V=VM
Z=ZM
C=CM
D=DM

```

```

E=EM
Y=B/(4.000*V)
IF(M.NE.1) GO TO 650
B1=BC
C1=CC
D1=DC
E1=EC
X1=XC
X2=XW
GO TO 660
650 B1=BW
C1=CW
D1=DW
E1=EW
X1=XW
X2=XC
660 FCM=(4.000*Y-3.000*Y*Y)/((1.000-Y)**2)
FCM=FCM+((B1/B)*((4.000*Y-2.000*Y*Y)/((1.000-Y)**3)))
FCM=FCM-(((2.000*C1*X1+2.000*CIJ*X2)/(RT*B))*(DLOG((V+B)/V)))
FCM=FCM-((C*B1)/(RT*B*(V+B)))
FCM=FCM+(((C*B1)/(RT*B*B))*(DLOG((V+B)/V)))
FCM=FCM-((2.000*D1*X1+2.000*DIJ*X2+D)/(RT*V*B))
FCM=FCM+(((2.000*X1*D1+2.000*DIJ*X2+D)/(RT*B*B))*(DLOG((V+B)/V)))
FCM=FCM+((D*B1)/(RT*V*B*(V+B)))
FCM=FCM+((2.000*B1*D)/(RT*B*B*(V+B)))
FCM=FCM-(((2.000*B1*D)/(RT*(B**3)))*(DLOG((V+B)/V)))
FCM=FCM-((2.000*E1*X1+2.000*EIJ*X2+2.000*E)/(RT*2.000*B*V*V))
FCM=FCM+((2.000*E1*X1+2.000*EIJ*X2+2.000*E)/(RT*B*B*V))
FCM=FCM-(((2.000*E1*X1+2.000*EIJ*X2+2.000*E)/(RT*(B**3)))*(DLOG((V
1+B)/V)))
FCM=FCM+((E*B1)/(RT*2.000*B*V*V*(V+B)))
FCM=FCM-((3.000*E*B1)/(RT*2.000*B*B*V*(V+B)))
FCM=FCM+(((3.000*E*B1)/(RT*(B**4)))*(DLOG((V+B)/V)))
FCM=FCM-((3.000*E*B1)/(RT*(B**3)*(V+B)))
FCM=FCM-(DLOG(Z))
FCM=DEXP(FCM)
IF(M.NE.1) GO TO 670
FCCM=FCM
GO TO 699
670 FCWM=FCM
699 RETURN
END

```

INPUT THERMODYNAMIC DATA

41.46	0.0	2.2688	44.603	0.037754
0.0	0.0	-1001800.0	QUARTZ	
82.30	0.0	4.409	303.9	-.01339
0.0	-2904.3	-895200.0	KYANITE	
91.38	0.0	5.153	290.4	-0.01052
0.0	-2627.8	-1109000.0	ANDALUSITE	
95.77	0.0	4.99	226.1	0.01407
0.0	-1376.0	-2440000.0	SILLIMANITE	
201.79	0.0	10.079	516.83	-0.092492
.000041883	-4588.5	-1408500.0	ANORTHITE	
232.88	0.0	10.905	693.37	-0.1717
.000049188	-8305.4	3462200.0	SANIDINE	
143.09	0.0	6.609	191.82	0.083079
-0.0000217180.0		-4279500.0	DIOPSIDE	
66.03	0.0	3.147	350.68	-0.14725
0.000058264	-4295.7	1678900.0	ENSTATITE	
266.27	0.0	11.327	544.97	0.02068
0.0	-2274.63	-8329926.0	PYROPE	
260.12	0.0	12.53	516.35	0.03218
0.0	-1403.1	-9942021.0	GROSSULAR	
548.9	0.0	27.292	6131.0	-4.189
0.0017568	-85656.0	51385000.0	TREMOLITE	
287.89	0.0	14.071	917.67	-0.08111
0.0	-10348.0	2834100.0	MUSCOVITE	
260.33	0.0	13.625	534.3	0.037416
0.0	-2153.2	-8805200.0	TALC	
91.71	0.0	3.6934	99.715	0.02692
0.0	0.0	-2157600.0	CALCITE	
81.69	0.0	3.993	200.8	-0.0259
0.000007435	-1826.0	-157900.0	WOLLASTONITE	
188.83	0.0	0.0	7.368	0.027468
-.0000048117361.74		-223160.0	STEAM	
213.79	0.0	0.0	87.820	-0.0026442
0.0	-998.86	706410.0	CO2	
337.10	0.0	14.991	955.940	-0.08560
0.0	-10522.0	3345450	PHLOGOPITE	
50.92	0.0	2.5575	157.36	0.00071899
0.0	-988.04	-1896900.0	CORUNDUM	
95.19	0.0	4.379	227.98	0.0034139
0.0	-1744.6	-893970.0	FORSTERITE	
155.18	0.0	6.434	547.88	-0.16759
0.000077076	-6547.9	2840000.0	DOLOMITE	
465.26	0.0	20.711	1221.8	-0.05059
-.0000048117-10961.5		-2398110	CHLORITE	
82.0	0.0	3.971	222.91	0.0061267
0.0	-1551.2	-1685700.0	SPINEL	
295.85	0.0	13.59	697.52	0.013263
0.0	-5317.9	-3794100	ZOISITE	
129.20	0.0	5.565	176.73	0.023852
0.0	0.0	-3990500.0		
50.29	0.0	1.882	63.079	0.011307
0.0	-5.616	-986260.0		

INPUT DATA
5 (NO OF PHASES INVOLVED)
22 -1
20 1
3 2
23 1 (NO OF PHASE IN THERMO DATA LISTING & REACTION COEFFICIENT)
17 4
1
0 4 (REACTION COEFFICIENTS OF XCO2 AND H2O)
336200.01.0 (ENTHALPY OF REACTION AT 298 & EQUILIBRIUM CONSTANT)
2.00 300.00 0.00 1 (P,T ESTIMATE, XCO2 & 1 INDICATES NEW REACTION)

TO CALCULATE P-T PATHS FROM ZONING PROFILES IN GIVEN ASSEMBLAGES

This program utilises the method of Spear and Selverstone (1983) to calculate P-T paths for rocks containing suitable assemblages. The program calculates coefficients for a set of linear differential equations, resulting in the matrix AA where $AA.X=0$, where AA is the matrix of coefficients and X contains differentials (see Spear and Selverstone, 1983). In order to produce a solution certain differentials must be held constant. This is accomplished using the subroutine MPREP which omits selected columns of AA and interchanges appropriate rows. This results in the matrix equation: $A.X=Y$. This set of linear equations is solved using the NAG library subroutine F04ATF. Volumes of H_2O are calculated from the subroutine VOLCALC, which utilises the MHSRK equation of Kerrick and Jacobs (1981). The program requires repeated solutions of the set of linear equations. For this purpose changes in composition are divided into eight increments. For each increment the partial differentials are evaluated using compositions, pressure and temperature halfway between the ends of the increment. Recalculation of the pressure, temperature and compositions at the end of the increment is repeated until successive iterations differ by less than $1^\circ C$ and 10bars.

PROGRAM LISTING

List of arrays used : AA-Set of coefficients for system of linear equations
 A-AA with appropriate columns and rows omitted.
 Y-Matrix Y where A.X=Y
 C-solution for X for A.X=Y
 JQE-indicates which rows of AA should be omitted
 N-No. of sites for mixing
 JQP, S & V-store information on each phase component
 CO & COP-compositions of phases
 TX & PX partial differentials of P & T
 GG-stores partial differentials of X
 WKS1, WKS2 & AF- workspaces for subroutine F04ATF

```

C PROGRAM TO CALCULATE P-T PATHS GIVEN MINERAL ZONING DATA
C SEE SPEAR AND SELVERSTONE (1983):CONTRIB.MINERAL.PETROL.
C INPUT PARAMETERS
C IMPLICIT REAL*8(A-H,P,R-Z)
C DIMENSION JQH(14),N(14),JQP(20,4),S(20),V(20),CO(20,8),AA(28,28)
C DIMENSION P(8),T(8),VZ(15),JQCO(7),COP(18),TX(6),PX(6),A(24,24)
C DIMENSION Y(24),JQE(27),AF(29,29),WKS1(29),WKS2(29),C(28)
C DIMENSION GG(5,5),KPN(5)
C READ(5,11)JQ,JQC,JQS
C JQ/NO OF PHASES, JQC/NO OF PHASE COMPONENTS, JQS/NO OF SYSTEM
C COMPONENTS, JQR/NO OF INDEPENDENT EQUILIBRIUM CONDITIONS
C JQV/NO OF MONITOR DXI, JQX/NO OF INDEPENDENT NON MONITORING
C DXI
C JQR=JQC-JQS
C JQV=JQC-JQ-JQR+2
C JQL/NO OF COLUMNS, JQN/NO OF ROWS IN AA
C JQL=2+(2*JQC)-JQ
C JQN=JQR+JQC
C JQX=JQR-2
C DO 100 I=1,JQ
C READ(5,12)JQH(I),N(I)
C JQH/NO OF PHASES, N/NO OF SITES FOR MIXING
100 CONTINUE
C DO 200 I=1,JQC
C READ(5,13)JQP(I,1),JQP(I,2),JQP(I,3),JQP(I,4),S(I),V(I)
C JQP(I,1)/NO OF PHASE COMPONENT, JQP(I,2)/NO OF PHASE TO WHICH BELONGS
C 3/1 IF MONITOR 0 IF NOT, 4/1 IF INDEPENDENT 0 IF NOT
C S/ENTROPY OF COMPONENT, V/VOLUME OF COMPONENT

```

```

      READ(5,14)CO(I,1)
      READ(5,14)CO(I,3)
C     INPUT INITIAL AND FINAL COMPOSITIONS
200  CONTINUE
      DO 300 I=1,JQR
      DO 250 JI=1,JQC
      IJ=I+JQ
      IIJ=II+2
      READ(5,15)JAA
      AA(IJ,IIJ)=FLOAT(JAA)
C     II/PHASE COMPONENT COEFFICIENT, I/NO OF REACTION
250  CONTINUE
300  CONTINUE
C     INPUT INITIAL PRESSURE IN BARS AND TEMP IN DEG. CENTIGRADE
      READ(5,16)P(1),T(1)
      T(1)=T(1)+273.1500
C     INPUT INITIAL P&T
      JJQ=1
C     CALCULATE INTERIOR COMPOSITIONS FOR MONITORING COMPONENTS
      DO 400 I=1,JQC
      DO 412 J=1,7
      KF=J+1
      CO(I,KF)=CO(I,J)+((CO(I,3)-CO(I,1))/7)
412  CONTINUE
400  CONTINUE
C     RUN THE REMAINDER OF THE PROGRAM FOR EACH OF 7 INCREMENTS. FOR EACH
C     INCREMENT THE PROGRAM CALCULATES THE PARTIAL DIFFERENTIALS OF P AND
C     T AND OF NON MONITORING INDEPENDENT COMPONENTS. DURING THE FIRST
C     ITERATION THESE ARE CALCULATED AT THE INITIAL P, T AND COMPOSITION
C     DURING SUBSEQUENT ITERATIONS THE DIFFERENTIALS ARE CALCULATED AT
C     THE PRESSURE, TEMPERATURE AND COMPOSITIONS WHICH ARE THE AVERAGE
C     OF THE VALUES AT THE BEGINNING AND AT THE END OF THE INCREMENT. WHEN
C     SUBSEQUENT ITERATIONS PRODUCE FINAL VALUES OF P & T WHICH DIFFER
C     BY LESS THAN 1 DEG AND 5 BARS THEN P AND T ARE OUTPUT.
9940 DO 9999 NNF=1,7
      NNG=NNF+1
9941 IF(IZZ.GT.700) GO TO 106
      IZZ=IZZ+1
      IF(IIS.EQ.0) GO TO 697
      DO 9997 IPZ=1,JQC
      COP(IPZ)=0.500*(CO(IPZ,NNF)+CO(IPZ,NNG))
9997 CONTINUE
      TT=0.500*(T(NNF)+T(NNG))
      PP=0.500*(P(NNF)+P(NNG))
      GO TO 699
697  PP=P(NNF)
      TT=T(NNF)
      DO 699 IPZ=1,JQC
      COP(IPZ)=CO(IPZ,NNF)
699  CONTINUE
C     CALCULATION OF MATRIX ELEMENTS AS FUNCTION OF P,T,X
C     THESE ELEMENTS FORM PART OF THE MATRIX AA. THE EQUATION AA.X=0
C     COMPRISES A GIBBS-DUHEM EQUATION FOR EACH PHASE, ALL THE INDEPENDENT
C     EQUILIBRIUM CONSTRAINTS AND EQUATIONS INTRODUCING ALL THE INDEPENDENT
C     COMPOSITIONAL VARIABLES FOR EACH PHASE
      II=1
      DO 500 LF=1,JQC
      LZ=LF+2
      IF(JQP(LF,2).EQ.II) GO TO 700
      GO TO 710
700  VA=VA+(COP(LF)*V(LF))

```

```

AA(II,LZ)=COP(LF)
706 SA=SA+(COP(LF)*S(LF))-N(II)*8.314300*COP(LF)*(DLOG(COP(LF)))
IF(LF.EQ.JQC) GO TO 710
GO TO 500
710 AA(II,2)=-VA
AA(II,1)=SA
VA=0.0
SA=0.0
II=II+1
IF(LF.EQ.JQC) GO TO 500
AA(II,LZ)=COP(LF)
VA=COP(LF)*V(LF)
DO 333 IID=1,JQC
333 CONTINUE
SA=(COP(LF)*S(LF))-N(II)*8.314300*COP(LF)*(DLOG(COP(LF)))
II/COUNTS PHASES
500 CONTINUE
CALCULATION OF TERMS IN COMPOSITIONAL DERIVATIVE EQUATIONS
JQRE=JQ+JQR+1
MG=2+JQC+1
JQRH=JQRE+JQV
MRH=MG+JQV
IJ=0
II=1
MJ=JQV+1
DO 1000 LM=1,JQC
31 IF(JQP(LM,2).EQ.II) GO TO 35
GO TO 300
35 IJ=IJ+1
JQCO(IJ)=JQP(LM,1)
IF((JQP(LM,4)).EQ.0) GO TO 798
IF(JQP(LM,3).EQ.1) GO TO 41
GO TO 799
41 KZ=1
GO TO 799
798 K=JQCO(IJ)
799 IF(LM.EQ.JQC) GO TO 300
GO TO 1000
500 IF(IJ.EQ.1) GO TO 999
IF(KZ.EQ.1) GO TO 817
MRJ=MRH+IJ-2
MRG=MRH
GO TO 818
817 MJ=MG+IJ-2
MH=MG
818 DO 820 L=1,IJ
M=JQCO(L)
IF(K.EQ.M) GO TO 820
KK=K+2
MM=M+2
IF(KZ.EQ.1) GO TO 807
GO TO 805
807 AA(JQRE,1)=-S(K)+S(M)+(N(II)*8.31400*(DLOG(COP(K))-
1 DLOG(COP(M))))
AA(JQRE,2)=V(K)-V(M)
AA(JQRE,KK)=-1.000
AA(JQRE,MM)=1.000
AA(JQRE,MG)=-N(II)*8.31400*TT*((1/COP(M))+(1/COP(K)))
DO 305 JQI=MH,MJ
IF(JQI.EQ.MG) GO TO 305
AA(JQRE,JQI)=-N(II)*8.31400*TT*(1/(COP(K)))

```

```

805 CONTINUE
  JQRE=JQRE+1
  MG=MG+1
  GO TO 320
808 AA(JQRH,1)=-S(K)+S(M)+(N(II)*8.314300*(DLOG(COP(K))-
1 DLOG(COP(M))))
  AA(JQRH,2)=V(K)-V(M)
  AA(JQRH,KK)=-1.000
  AA(JQRH,MM)=1.000
  AA(JQRH,MRH)=-N(II)*8.314300*TT*((1/COP(M))+(1/COP(K)))
  DO 809 JQF=MRG,MRJ
  IF(JQF.EQ.MRH) GO TO 809
  AA(JQRH,JQF)=-N(II)*8.314300*TT*(1/(COP(K)))
809 CONTINUE
  JQRH=JQRH+1
  MRH=MRH+1
820 CONTINUE
999 IF(LM.EQ.JQC) GO TO 1000
  IJ=0
  II=II+1
  KZ=0
  GO TO 31
1000 CONTINUE
C   WATER IS ALWAYS PHASE NUMBER 4 IN THE INPUT DATA. THE SUBROUTINE
C   VOLCALC IS CALLED TO CALCULATE THE VOLUME OF H2O (AND ALSO OF CO2
C   IF REQUIRED AND THE PROG IS MODIFIED) AT THE P & T OF INTEREST
C   THE SUBROUTINE UTILISES THE MHSRK EQUATION OF KERRICK AND
C   JACOBS AND IS A MODIFICATION OF PART OF THEIR PROGRAM
  CALL VOLCALC(PP,TT,VC,VW)
  AA(4,2)=-VW/10.000
C   CALCULATE DT/DXI
C   THE PARTIAL DIFFERENTIAL OF T W.R.T. EACH OF THE MONITORING COMPONENTS
C   IS CALCULATED. APPROPRIATE VARIABLES ARE HELD CONSTANT BY OMITTING
C   APPROPRIATE COLUMNS, INDICATED BY THE VALUE OF JQE(I) WHERE I IS
C   THE ROW NUMBER. THIS MANIPULATION IS ACCOMPLISHED USING THE
C   SUBROUTINE MPREP
  JQZZ=JQ+JQR+JQV
  JQE(1)=1
  JQE(2)=0
  JQCC=JQC+2
  DO 3500 J=3,JQCC
  JQE(J)=0
3500 CONTINUE
  MND=JQC+2+JQV+JQX
  MNE=MND-JQX
  IFAIL=0
  IA=24
  NZ=JQC+2
  IAA=26
  JQQ=JQCC+1
  DO 747 IQQ=JQQ,MND
  JQE(IQQ)=2
747 CONTINUE
  DO 4000 NJ=JQQ,MNE
  JQE(NJ)=0
  LX=LX+1
  IIS=1
  IFF=0
  CALL MPREP(JQE,AA,A,Y,JUN,JQL,IFF,INR,JHP)
C   THE SUBROUTINE MPREP RETURNS THE MATRICES A AND Y WHERE A.X=Y
C   AND THE NUMBER OF COLUMNS OF A EQUALS THE NUMBER OF ROWS

```

SOLUTION OF THESE EQUATIONS IS ACCOMPLISHED USING THE NAG LIBRARY
 SUBROUTINE F04ATF. THIS RETURNS A MATRIX C WHICH CONTAINS THE SOLUTION
 CALL F04ATF(A,IA,Y,NZ,C,AF,IAA,WKS1,WKS2,IFAIL)
 IF(IFAIL.EQ.0) GO TO 433
 GO TO 5000

433 CONTINUE

TX(LX)=1/C(JQCC)
 WRITE(3,33)TX(LX)
 JQE(NJ)=2

4000 CONTINUE

LX=0
 CALCULATE DP/DXI ACCOMPLISHED SIMILARLY TO DIFF. OF T W.R.T XI
 JQE(1)=0
 JQE(2)=1
 DO 4500 J=3,JQCC

JQE(J)=0

4500 CONTINUE

DO 847 IQQ=JQQ,MND
 JQE(IQQ)=2

847 CONTINUE

DO 5000 NJ=JQQ,MNE
 JQE(NJ)=0

CALL MPREP(JQE,AA,A,Y,JQN,JQL,IFF,INR,JHP)
 CALL F04ATF(A,IA,Y,NZ,C,AF,IAA,WKS1,WKS2,IFAIL)
 IF(IFAIL.EQ.0) GO TO 533
 GO TO 5000

533 CONTINUE

LX=LX+1
 PX(LX)=1/C(JQCC)
 WRITE(3,33)PX(LX)
 JQE(NJ)=2

5000 CONTINUE

LX=0
 DO 3333 MIZ=1,JQC
 IF(JQP(MIZ,3).EQ.1) GO TO 3222
 GO TO 3333

3222 MIX=MIX+1

DT=TX(MIX)*(CO(MIZ,NNG)-CO(MIZ,NNF))+DT
 DP=PX(MIX)*(CO(MIZ,NNG)-CO(MIZ,NNF))+DP

3333 CONTINUE

P(NNG)=P(NNF)+DP
 T(NNG)=T(NNF)+DT
 WRITE(6,33)T(NNG)
 WRITE(6,33)P(NNG)

IIS=1

MIX=0

DT=0.000

DP=0.000

ICP=1

IFF=1

INR=15

C CALCULATION OF COMPOSITIONAL DERIVATIVES OF INDEPENDENT NON

C MONITORING COMPONENTS W.R.T. T AND X(J)

C NEXT SECTION SELECTS NON MONITORING INDEPENDENT PHASE COMPONENTS

7197 DO 7009 IFK=1,JQC

IF(JQP(IFK,2).GT.JZD) GO TO 3334

GO TO 7009

3334 IF(JQP(IFK,3).EQ.0 .AND. JQP(IFK,4).EQ.1) GO TO 7240

7009 CONTINUE

GO TO 7230

7240 JQE(1)=1

```

JQE(2)=0
JZD=JQP(IFE,2)
JHZ=0
DO 7242 IFE=1,JQC
IF(JQP(IFE,3).EQ.0) GO TO 7243
GO TO 7242
7243 IF(JQP(IFE,2).EQ.JZD) GO TO 7244
GO TO 7242
7244 IF(JQP(IFE,4).EQ.1) GO TO 7246
GO TO 7242
7246 JHZ=JHZ+1
7242 CONTINUE
DO 7250 IG=3,JQCC
JQE(IG)=0
7250 CONTINUE
IC0=1
INO=JQCC+JQV+IC0+JHP
IVO=INO+1+JHZ-1
DO 7260 IQ=JQQ,MND
JQE(IQ)=2
7260 CONTINUE
DO 7262 IVF=INO,IVO
JQE(IVF)=0
7262 CONTINUE
INR=JQZZ
CALL MPREP(JQE,AA,A,Y,JQN,JQL,IFF,INR,JHP)
JFZ=JQC+3
NZ=JQC+JHZ+1
CALL F04ATF(A,IA,Y,NZ,C,AF,IAA,WKS1,WKS2,IFAIL)
IF(IFAIL.EQ.0) GO TO 7261
GO TO 7230
7261 CONTINUE
DO 7777 IFD=1,MND
JQE(IFD)=2
7777 CONTINUE
IPD=JHZ
LBF=JQCC
C THE ARRAY GG STORES DERIVATIVES OF X(J) W.R.T. T AND X(I)
C WHERE X(J) ARE INDEPENDENT NON MONITORING PHASE COMPONENTS
C AND X(I) ARE MONITORING PHASE COMPONENTS
DO 7007 IHQ=1,IPD
IHZ=IHQ+JHP
GG(1,IHZ)=C(LBF)
LBF=LBF+1
7007 CONTINUE
C CALCULATE COMPOSITIONAL DERIVATIVES W.R.T. OTHER COMPOSITIONAL
C PARAMETERS
JQE(1)=2
JQPP=JQC+3
JZA=2+JQC+JQV
DO 7285 LXX=JQPP,JZA
JQE(LXX)=1
ICP=ICP+1
CALL MPREP(JQE,AA,A,Y,JQN,JQL,IFF,INR,JHP)
CALL F04ATF(A,IA,Y,NZ,C,AF,IAA,WKS1,WKS2,IFAIL)
IF(IFAIL.EQ.0) GO TO 7284
GO TO 7230
7284 CONTINUE
LBF=JQCC
DO 7013 IGX=1,IPD
IGQ=IGX+JHP

```

```

      GG(ICP,IGQ)=C(LBF)
      LBF=LBF+1
7013 CONTINUE
      JQE(LXX)=2
7285 CONTINUE
7286 CONTINUE
      ICP=1
C     CALCULATION OF CHANGE IN COMPOSITION OF INDEPENDENT NON MONITORING
C     PHASE COMPONENTS
C     THE NECESSARY PARTIAL DIFFERENTIALS ARE STORED IN THE ARRAY GG
C     THE SECTION SELECTS PHASE COMPONENTS CORRESPONDING TO ELEMENTS
C     OF GG AND CALCULATES THE NEW COMPOSITIONS OF PHASES OF VARIABLE
C     COMPOSITION
      IJY=1
      DO 7208 KKA=1,IPD
      KKB=KKA+JHP
      DX=GG(1,KKB)*(T(NNG)-T(NNF))
      IF(JQV.LT.2) GO TO 7213
      DO 7219 IKR=1,JQC
      IF(JQP(IKR,3).EQ.1 .AND. JQP(IKR,4).EQ.1) GO TO 7217
      GO TO 7219
7217 IJY=IJY+1
      DX=DX+(GG(IJY,KKB)*(CO(IKP,NNG)-CO(IKR,NNF)))
7219 CONTINUE
      IJY=1
7218 DO 7220 JKH=1,JQC
      IF(JQP(JKH,2).EQ.JZD) GO TO 7437
      GO TO 7220
7437 IF(JQP(JKH,3).EQ.0 .AND. JQP(JKH,4).EQ.1) GO TO 7221
      GO TO 7220
7221 IFG=IFG+1
      IF(IFG.EQ.KKB) GO TO 7222
      GO TO 7220
7222 CO(JKH,NNG)=CO(JKH,NNF)+DX
      IFG=0
      DX=0.000
      GO TO 7208
7220 CONTINUE
7208 CONTINUE
      DO 5345 IXB=1,5
      WRITE(3,19)GG(IXB,1),GG(IXB,2),GG(IXB,3),GG(IXB,4),GG(IXB,5)
5345 CONTINUE
      19 FORMAT(5F15.8)
      DX=0.000
      DO 7239 IXF=1,5
      DO 7233 IXG=1,5
      GG(IXF,IXG)=0
7233 CONTINUE
7239 CONTINUE
      DO 7201 IBB=INO,IVO
      JQE(IBM)=2
7201 CONTINUE
      JHP=JHP+JHZ
      GO TO 7197
7230 CONTINUE
      JZD=0
      JHP=0
      JHZ=0
      ICO=0
      CALCULATION OF ALL DEPENDENT COMPOSITIONAL PARAMETERS
      DO 8230 IF=1,JQC

```

```

      IF(JQP(IF,3).EQ.1) GO TO 8230
      IF(JQP(IF,4).EQ.1) GO TO 8230
      KY=JQP(IF,2)
      DO 8229 IG=1,JQC
      IF(IG.EQ.IF) GO TO 8223
      IF(JQP(IG,2).EQ.KY) GO TO 8222
      GO TO 8223
8222 COZ=COZ+CO(IG,NNG)
8223 CONTINUE
8229 CONTINUE
      CO(IF,NNG)=1.000-COZ
      COZ=0.000
8230 CONTINUE
C     IF FINAL P & T IS SUFFICIENTLY CLOSE TO THE PREVIOUS ITERATION THEN
C     WRITE P & T AND CONTINUE TO THE NEXT INCREMENT. IF DESIRED FOR GREATER
C     ACCURACY THE NUMBER OF INCREMENTS MAY BE INCREASED AND THE MAXIMUM
C     VALUES OF PD AND TD REDUCED.
      PD=DABS(P(NNG)-PF)
      TD=DABS(T(NNG)-TF)
      IF(PD.LT.5.000) GO TO 9950
      GO TO 9954
9950 IF(TD.LT.1.000) GO TO 9960
9954 PF=P(NNG)
      TF=T(NNG)
      GO TO 9941
9960 IIS=0
      WRITE(3,59)P(NNG),T(NNG)
      DO 7011 KXY=1,JQC
      WRITE(3,59)CO(KXY,NNG),CO(KXY,NNG)
7011 CONTINUE
9999 CONTINUE
106  CONTINUE
      59 FORMAT(2F14.3)
      20 FORMAT(2I4,F12.3)
      11 FORMAT(3I3)
      12 FORMAT(2I3)
      13 FORMAT(4I3,2F6.0)
      14 FORMAT(F6.4)
      15 FORMAT(13I3)
      38 FORMAT(F15.5)
      16 FORMAT(2F6.0)
      STOP
      END

```

```

SUBROUTINE MPREP(JQE,AA,A,Y,JQN,JQL,IFF,INR,JHP)
IMPLICIT REAL*8(A-H,P,R-Z)
DIMENSION JQE(24),AA(25,25),A(24,24),Y(24),AB(25,25)
C   OMITTS COLUMNS JQE(I) WH I=1,2
C   Y GIVEN BY COLUMN INDIC BY JQE(I)=1
C   RETAINS COLUMNS JQE(I)=0
C   IF IFF DOES NOT EQUAL 0 INR TH ROW IS OMITTED
C   AND REPLACED BY INX TH AND INR+1 TH BY INX+1 TH ETC.
DO 2966 IAB=1,25
DO 2967 IAC=1,25
  AB(IAC,IAB)=AA(IAC,IAB)
2967 CONTINUE
2966 CONTINUE
  IF(IFF.EQ.0) GO TO 2969
  DO 7000 IQS=INR,24
  INX=IQS+1+JHP
  DO 2968 IQT=1,25
  AB(IQS,IQT)=AA(INX,IQT)
2968 CONTINUE
7000 CONTINUE
2969 IP=0
  DO 3000 I=1,JQL
  IF(JQE(I).EQ.1) GO TO 2950
  IF(JQE(I).EQ.2) GO TO 2950
  IP=IP+1
  DO 2970 J=1,JQN
  A(J,IP)=AB(J,I)
2970 CONTINUE
2950 CONTINUE
  IF(JQE(I).EQ.1) GO TO 2990
  GO TO 3000
2990 DO 2995 L=1,JQN
  Y(L)=-AB(L,I)
2995 CONTINUE
3000 CONTINUE
  RETURN
  END

```

```

SUBROUTINE VOLCALC(P,T,VC,VW)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
COMMON /MNRVAR/PK,R,T12
R=83.14D0
BW=29.00D0
BC=58.00D0
PK=P/1000.00D0
T12=DSQRT(T)
T15=DSQRT(T**3)
RT=R*T15
CC=(28.31D0+0.10721D0*T-0.00000331D0*T*T)*1000000.00D0
DC=(9380D0-8.53D0*T+0.001189D0*T*T)*1000000.00D0
EC=(368654.00D0+715.9D0*T+0.1534D0*T*T)*1000000.00D0
CW=(290.78D0-0.30276D0*T+0.00014774D0*T*T)*1000000.00D0
DW=(-8374.0D0+19.437D0*T-0.003143D0*T*T)*1000000.00D0
EW=(76600.00D0-133.9D0*T+0.1071D0*T*T)*1000000.00D0
TC=T-273.15D0
DO 300 J=1,2
CALL ZPURE (PK,ZC,VC,ZW,VW,TC)
300 CONTINUE
RETURN
END
SUBROUTINE ZPURE(PK,ZC,VC,ZW,VW,TC)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MVAR/BC,CC,DC,EC,BW,CW,DW,EW,J,L,M
SUBROUTINE FROM PAPER OF JACOBS AND KERRICK (1931)
SEE COMPUTERS IN GEOLOGY (1961)

```

```

IF(J.NE.1) GO TO 210
S=BC
C=CC
D=DC
E=EC
IF(PK.GE.1.000)VI=35.00
IF(PK.GE.0.1000 .AND. PK.LT.1.000) VI=100.0000
IF(PK.GE.0.00500 .AND. PK.LT.0.1000) VI=500.00
IF(PK.LT.0.00500) VI=50000.0
GO TO 250
210 B=BW
C=CW
D=DW
E=EW
IF(PK.GE.1.000) VI=15.0
IF(PK.GE.0.6000 .AND. PK.LT.1.000) VI=22.50
IF(PK.GE.0.2100 .AND. PK.LT.0.6000 .AND. TC.GE.550.000)VI=5.00
IF(PK.GE.0.2100 .AND. PK.LT.0.6000 .AND. TC.LT.550.000) VI=35.00
IF(PK.GE.0.1000 .AND. PK.LT.0.2100 .AND. TC.LT.400.000) VI=15.00
IF(PK.GE.0.1000 .AND. PK.LT.0.2100 .AND. TC.GE.400.000) VI=100.00
IF(PK.GE.0.00500 .AND. PK.LT.0.1000) VI=500.00
IF(PK.LT.0.00500) VI=7000.0
250 CALL NEWRAP(B,C,D,E,Z,V,VI)
IF(J.NE.1) GO TO 260
ZC=Z
VC=V
GO TO 299
260 ZW=Z
VW=V
299 RETURN
END
SUBROUTINE NEWRAP(B,C,D,E,Z,V,VI)
IMPLICIT REAL*8(A-H,P,R-Z)
COMMON /MNRVAR/PK,P,T,R,T12
DO 350 K=1,50
Y=B/(4.000*VI)
X=(1.000-Y)
BI=(VI+B)
BI2=(VI+B)**2
PN=1.000+Y+(Y**2)-(Y**3)
PR=(PN/(VI*(X**3)))*R*T
PA1=C+(D/VI)+(E/(VI*VI))
PA2=PA1/(T12*VI*BI)
F=PR-PA2-P
D1=(-3.000*B)/(4.000*(VI**3)*X**4)
D2=-1.000/((VI**2)*(X**3))
D3=1.000/(VI*(X**3))
D4=-B/(4.000*VI**2)
D5=-2.000*(B**2)/(16.000*(VI**3))
D6=3.000*(B**3)/(64.000*(VI**4))
DPR=((PN*(D1+D2))+(D3*(D4+D5+D6)))*R*T
D7=(-1.000/(VI*BI2))+(-1.000/(VI**2*BI))
D8=1.000/(VI*BI)
D9=(-D/VI**2)+((-2.000*E)/(VI**3))
DPA=(PA1*D7+D8*D9)/T12
DF=DPR-DPA
V=VI-(F/DF)
DIFF=DABS(V-VI)
IF(DIFF.LT.0.0100) GO TO 360
VI=V
350 CONTINUE
360 Z=(V*P)/(R*T)
RETURN
END

```

INPUT DATA

7	13	9	NO. PHASES, PHASE COMPONENTS,			
1	1		AND SYSTEM COMPONENTS			
2	1					
3	1					
4	1					
5	3		PHASE AND NO. OF SITES			
6	6					
7	1					
1	1	0	0	41.34	2.27	JQP, ENTROPY, VOLUME
1.00						INITIAL AND FINAL COMPOSITIONS
1.00						
2	2	0	0	287.86	14.07	
1.00						
1.00						
3	3	0	0	83.68	4.410	
1.0						
1.0						
4	4	0	0	188.70	1500.	
1.0						
1.0						
5	5	1	1	1316.31	11.53	
0.78						
0.76						
6	5	1	1	1254.68	12.53	
0.06						
0.08						
7	5	1	1	1311.70	11.79	
0.02						
0.01						
8	5	0	0	255.91	11.31	
0.14						
0.15						
9	6	0	1	795.8	30.86	
0.520						
0.520						
10	6	0	1	841.0	31.84	
0.001						
0.001						
11	6	0	0	636.9	29.93	
0.479						
0.479						
12	7	1	1	205.4	10.08	
0.23						
0.23						
13	7	0	0	207.15	10.03	
0.77						
0.77						
2						

-2
4
0
0
0
0
-2
0
0
1
0
0
2
-2
4
0
-2
0
0
0
1
0
0
0
0
0
0
0
0
0
2
0
-2
0
-1
1
0
0
0
1
0
2
0
0
1
0
0
0
0
0
-3
0

REACTION COEFFICIENTS

6000. 650. PRESSURE AND TEMPERATURE