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ASPECTS OF LOW-GRADE METAMORPHISM IN

NORTHERN SNOWDONIA, WALES

VOLUME I

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#### ABSTRACT

The effects of low-grade metamorphism have been examined in the Lower Palaeozoic rocks of northern Snowdonia.

A variety of techniques have been utilised including:- bulk rock geochemistry, petrography and microprobe determinations of secondary phase chemistry in the widespread meta-dolerite intrusions; illite crystallinity determination and white mica  $b_0$  measurement in the argillaceous meta-sediments; and fluid inclusion analysis in vein quartz.

Meta-dolerite mineral assemblages and phase compositions indicate an increase in grade southwards with dominantly prehnite-pumpellyite facies assemblages in the northern, and lower greenschist facies assemblages in the central and southern, Conwy Valley. Meta-dolerite assemblages are less diagnostic in central northern Snowdonia.

The phyllosilicates reveal a sharp metamorphic break within northern Snowdonia with relatively high illite crystallinity (epizone) and  $b_0$  in the western Conwy Valley and relatively low illite crystallinity (anchizone) and  $b_0$  throughout the rest of northern Snowdonia. The boundary between the two areas is sharp and can be correlated, over parts of its length, with major Lower Palaeozoic faults.

Fluid inclusions contain relatively low salinity,  $\text{CO}_2$ -poor, liquid-vapour, aqueous solutions. Mean filling temperatures range from 157 - 194°C with a slight increase from north to south.

Pre- and syn-deformation metamorphic effects have been recognised in northern Snowdonia. Combination of data from different techniques indicates pre-deformation temperatures and pressures ranging from approximately 290°C and 1.4Kb in central northern Snowdonia to 325 -

345°C and 2Kb in the western Conwy Valley, marking the transition from the prehnite-pumpellyite to lower greenschist facies of low-grade metamorphism. These figures indicate a low pressure facies series of metamorphism. The metamorphic effects of Caledonian deformation are continued recrystallisation in both the meta-dolerites and meta-sediments and further, minor, quartz veining.

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## CHAPTER 1

### INTRODUCTION

#### 1.1. Study area

The area of study is situated in Gwynedd, North Wales, the location of which is shown in Figure 1.1. Included within the area is all of the Snowdonia National Park north of the Snowdon massif, plus an adjacent fringe to the north, along the North Wales coast, the west, around Llanberis and Bethesda, and the east, down the eastern side of the Conwy Valley. The general physiographic characteristics of the area are shown in Figure 1.2.

#### 1.2. Aims of the research

The original project, conceived by Dr P.A. Floyd and Dr G. Rowbotham was to examine aspects of low-grade metamorphism in the Lower Palaeozoic Welsh basin. Previous research in the Welsh basin (Floyd et al., 1976; Bevins, 1978; Bevins et al., 1981, Bevins and Rowbotham, 1983) identified widespread secondary hydrous Ca-Al silicate assemblages within the meta-basites indicative of prehnite-pumpellyite and lowest greenschist facies metamorphism. Also preliminary work had indicated that a transition from prehnite-pumpellyite to greenschist facies assemblages occurred over a relatively short distance from north to south within the Conwy Valley.

The initial aim of the project was a detailed examination of secondary mineral assemblages and phase compositions within the well exposed meta-dolerites of the Conwy Valley. It was hoped that work on low-grade assemblages might be extended by using other techniques applicable to lithologies other than meta-basites and thus extend the geographical area and scope of the study.

FIGURE 1.1. A map of Wales showing the location of the area of study.

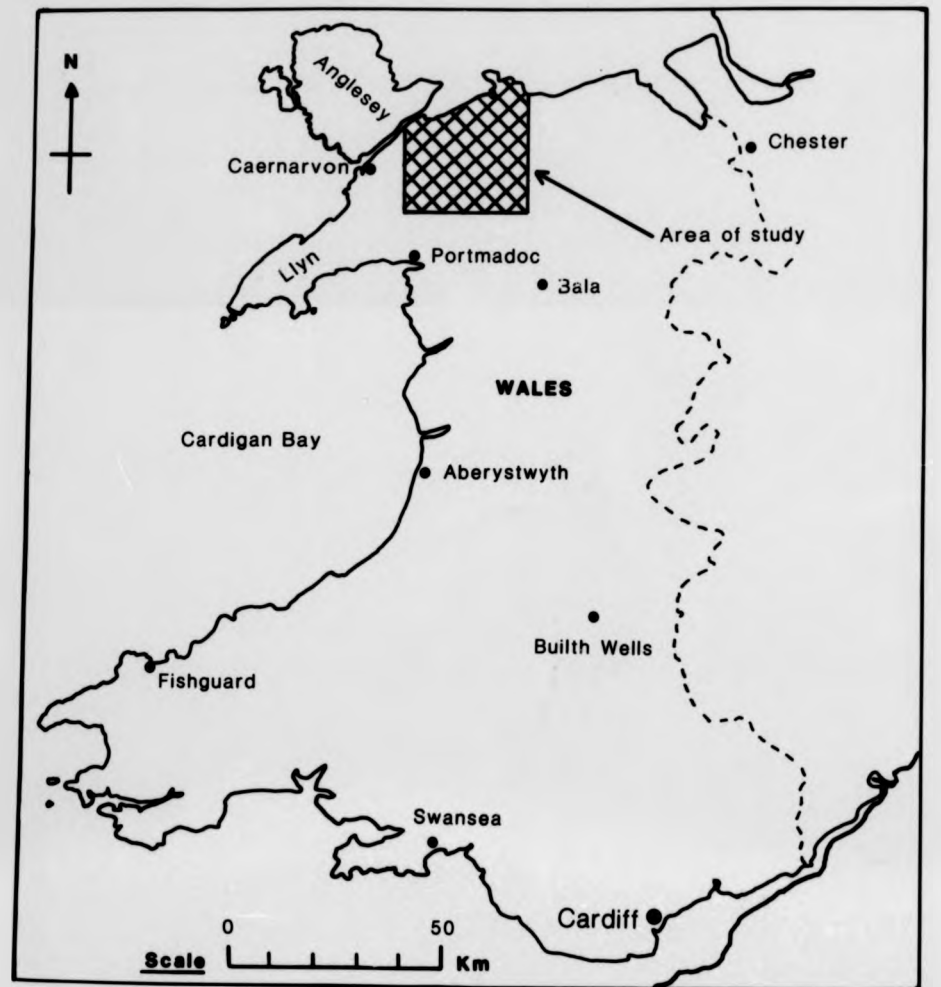
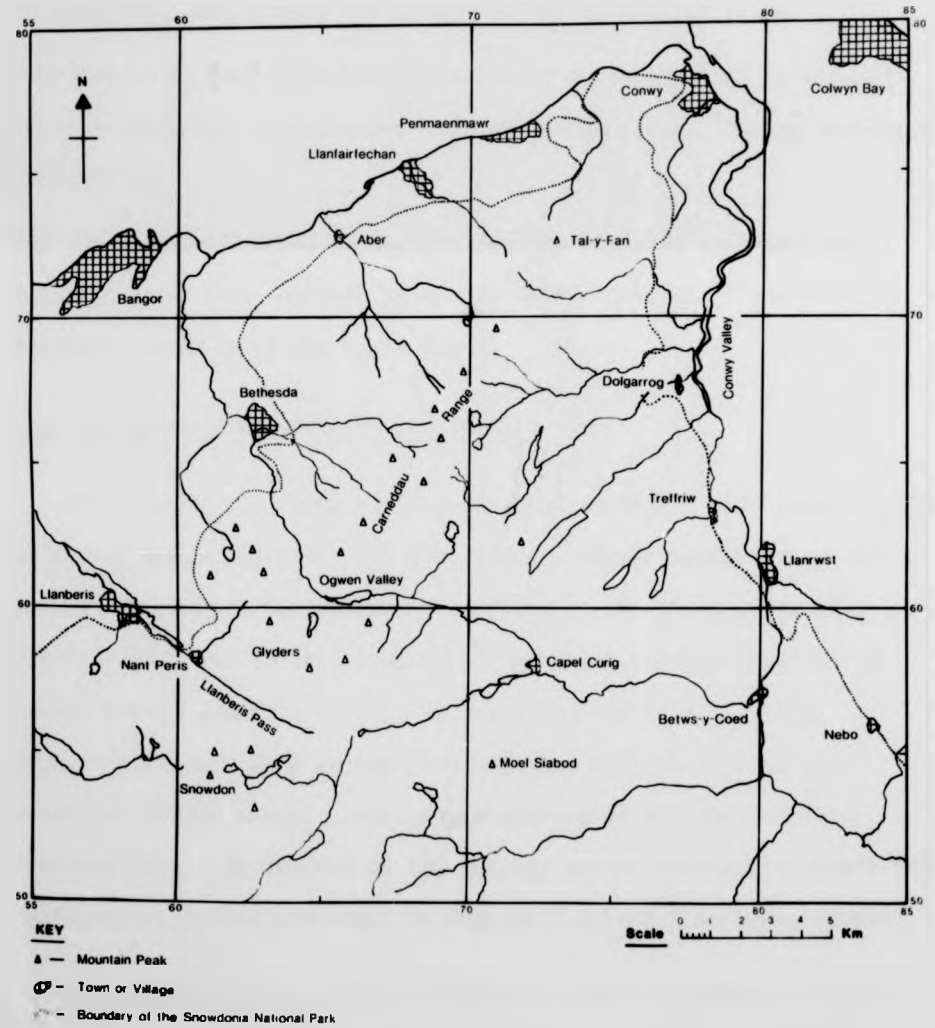


FIGURE 1.2. A map showing the general physiographic characteristics of northern Snowdonia.



The main objectives of the project were:-

- i) A detailed investigation of low-grade metamorphic phenomena in a critical area of the Welsh basin utilising meta-dolerite and metapelite secondary assemblages and vein quartz fluid inclusions.
- ii) Some quantification of the parameters of metamorphism particularly the pressure, temperature and nature of the associated fluid.
- iii) The relationship and relative timing of events such as mineral recrystallisation, deformation, vein emplacement, etc., during low-grade metamorphism.
- iv) To produce a model to account for the observed variation in metamorphism within northern Snowdonia in the context of the Lower Palaeozoic geology of the Welsh basin.

### 1.3. The geology of northern Snowdonia

As a result of a long history of detailed mapping and research the geology of North Wales is well documented. Recent summaries of the geology of northern Snowdonia can be found in the field guide of Roberts (1979) and in the accounts of the Dolgarrog and Capel Curig Special Sheets (Howells et al., 1978 and Howells et al., 1981a respectively) published by the then IGS (now BGS) as part of the resurveyed Bangor Sheet. Thus only a summary of the local geology is presented here. An outline of the geology of the area and a generalised stratigraphic column are shown in Figures 1.3. and 1.4. respectively.

The oldest rocks of the area are the Arvonian ignimbritic tuffs exposed on the Padarn ridge northwest of Llanberis. These tuffs conformably interdigitate with the overlying Fachwen Formation sediments of the lower Cambrian (Wood, 1969).

The middle-Lower Cambrian Llanberis Slates Formation consists of



FIGURE 1.3. A simplified geological map of northern Snowdonia, modified from Howells et al. (1978), Roberts (1979) and Howells et al. (1981a).

FIGURE 1.4. Generalised stratigraphy of northern Snowdonia from Howells et al. (1981b) and Reedman et al. (1983).

large amounts of mudstone with minor sandstones and are extensively exposed between Llanberis and Bethesda. They are thought to reflect stable sedimentation with the occasional influx of turbidity flows across the basin floor (Howells et al., 1981b). The overlying coarser turbiditic greywackes of the Bronllwyd Grit Formation and the black slates, siltstones and occasional sandstones of the Marchlyn Formation indicate a phase of active turbiditic sedimentation followed by a return to more stable sedimentation. The uppermost Cambrian sediments in the area are the Carnedd Y Filiast grits which display much bioturbation and contains numerous trace fossils indicating progressively shallower water deposition (Crimes, 1970). All Cambrian exposures are in the west of the area.

During the late Cambrian a period of regional uplift and erosion occurred resulting in a marked angular unconformity in northern Snowdonia. Reedman et al., (1983) discuss the Cambrian-Ordovician unconformity in some detail. In northern Snowdonia Carnedd Y Filiast grits are unconformably overlain by rocks of the Nant Ffrancon Formation. On the regional scale, the effects of this unconformity are greatest in the west and northwest. Kokelaar et al., (in press) relate the sub-Ordovician unconformity, and much of the variation in Cambrian sedimentation, to differential movement on major basement controlled block faults active throughout the Lower Palaeozoic. Webb (1983) describes an example of the control of contemporaneous faulting on sedimentation in the vicinity of Bethesda where the thickness of the Bronllwyd Grit Formation doubles across the Ffrydlas fault.

The Nant Ffrancon Formation represents the lowermost Ordovician and consists of shallow water bioturbated sandstones overlain by mudstones and siltstones. Occasional ironstone horizons indicate periodic shallowing. During the early Caradoc, sedimentation was

interrupted in northern Snowdonia by the onset of volcanic activity with the local production of seismically induced slump breccias. The Llewelyn Volcanic Group represents the first Caradoc volcanicity in the area. Volcanism was localised and only the Capel Curig Volcanic Formation can be traced throughout northern Snowdonia. Clearly, therefore, local stratigraphy must be highly variable even over short distances. Figure 1.5. (taken from Howells et al., 1983) demonstrates the stratigraphic complexity of the volcanic Caradoc sequences of North Wales. Sediments within the Llewelyn Volcanic Group contain structures indicative of shallow water and, locally, subaerial deposition (Francis and Howells, 1973).

The overlying Cwm Eigiau Formation marks a return to predominantly sedimentary conditions with only minor volcanism. The Pitts Head tuff occurs within the Cwm Eigiau Formation southwest of the Nant Ffrancon pass. Both the Llewelyn Volcanic Group and the Cwm Eigiau Formation thicken markedly towards the south. The top of the Cwm Eigiau Formation is typified by extensive tectonic instability marking renewed magmatic activity which produced the major volcanic sequences of northern Snowdonia, the Snowdon Volcanic Group and their equivalents to the northeast, the Crafnant Volcanic Group.

Magmatic doming resulted in marked, but local, unconformity beneath the Snowdon Volcanic Group. The lower Snowdon Volcanic Group consists of acid ash flow and pyroclastic material that is thickest around Snowdon and thins northeastwards. These are followed by bedded pyroclastics around Snowdon and the northern Conwy Valley and multiple-centred acid volcanism in the central Conwy Valley. The upper Snowdon/Crafnant Volcanic Group consists largely of acid ash flow material, although the basic Dolgarrog Volcanic Formation is locally developed in the central Conwy Valley. Associated sediments indicate a progressive

FIGURE 1.5. Stratigraphic variation in the Llewelyn Volcanic Group within northern Snowdonia, from Howells et al. (1983).

increase in water depth throughout the volcanic episode. The Caradoc volcanic sequences may again relate to major basement controlled faults active during the Lower Palaeozoic which played an important role in the accumulation and preservation of Lower Palaeozoic sequences in the Welsh basin (Beavon, 1963; Evans, 1968; Rast, 1969; Baker, 1971; Wood, 1974 and Kokelaar, 1979). The sediments above the main Caradoc volcanics are distinctive deep-water mudstones with occasional basic tuffs indicating continued minor volcanic activity. Towards the close of the Ordovician the sedimentary environment shallowed with turbiditic deposition of sandstones and siltstones.

Silurian strata are exposed around Conwy itself and down the eastern side of the Conwy Valley. The succession is volcanic free and sediments include striped mudstones, turbiditic sandstones and slumped units indicative of deposition in a rapidly subsiding basin.

Towards the end of the Silurian the major earth movements of the Caledonian Orogeny occurred. In north and central Wales three phases of deformation have been recognised (Helm et al., 1963; Roberts, 1967; Lynas, 1970; Fitches, 1972; Lynas, 1973). In North Wales the predominant structures are major F1, NE-SW trending, doubly plunging folds with an associated axial-planar slaty cleavage. Post-F1 structures in northern Snowdonia are represented by a late fracture cleavage and a suite of NW-SE trending folds, clearly exposed around Conwy, and identified by Roberts (1979) as F3 structures.

A large number of dolerites were intruded, particularly within the Ordovician volcanic horizons of the Conwy Valley. The age of the dolerites is uncertain and they have been variously described as pre- and post-deformation (Williams, 1927; Shackleton, 1954). Bromley (1969) suggested that there was a close temporal relationship between Caradoc volcanism and dolerite emplacement. Recently, Kokelaar et al. (in press)

have shown that many of the dolerites of Snowdonia display evidence of high level intrusion into wet sediments with the development of peperitic and pillowed margins. Kokelaar et al. (in press) show that at deeper levels within the Caradoc volcanic sequence the dolerites are thicker and coarser grained with progressive thinning and fining up the sequence. These observations clearly indicate that dolerite emplacement occurred during the Caradoc with the interaction of dolerite and wet host sediments and tuffs.

Recent reference lists detailing specific aspects of research within the Welsh basin and referring to much of the original map work and stratigraphic work can be found in the field guide to Snowdonia and Llyn (Roberts, 1979) and the recent paper by Kokelaar et al. (in press).

#### 1.4. History of research

##### 1.4.1. Low-grade metamorphism

Since the definition of the prehnite-pumpellyite facies by Coombs (1960) and the recognition of a prehnite-pumpellyite and pumpellyite-actinolite subfacies by Hashimoto (1966) much work has been done on the lower grades of metamorphism. Since this early work studies have been advanced by: i) recognition of other areas of low-grade metamorphism, ii) experimental and thermodynamic studies defining the stability fields of specific minerals and mineral assemblages, and iii) the development and adaptation of special techniques for studying low-grade rocks.

A large number of regional studies have been undertaken worldwide, particularly into secondary mineral assemblages and phase compositions developed within basic magmatic and volcanogenic rocks.

During the past 15 years experimental work (particularly by Liou and his co-workers in America) has investigated the stability and natural occurrence of many diagnostic low-grade secondary phases. As a result detailed information is now available for laumontite, wairakite and lawsonite (Liou, 1971a), epidote (Liou, 1973; Liou et al. 1983), pumpellyite (Schiffman and Liou, 1980) and prehnite (Liou, 1971b; Liou et al., 1983). Application of the experimental data to natural examples allows an estimation of the pressure, temperature and fluid chemistry of crystallisation.

Several workers have been developing or adapting techniques for the study of low-grade metamorphism. Over the past 20 years or so techniques such as illite crystallinity, fluid inclusion analysis, vitrinite reflectance, white mica  $b_0$  analysis, isotope geochemistry etc., have been extensively used.

Recently Kisch (1983a) has published a review paper summarising mineralogical reactions during the transition from diagenesis to metamorphism in clastic rocks. This paper refers to many of the regional studies undertaken before 1976. Kisch (1983b) also presents a literature review of work published between 1976 and 1982 as an appendix to this review paper.

#### 1.4.2. Metamorphism of the Welsh basin

Because of the low-grade of metamorphism within the Welsh basin relative to the rest of the Caledonides it is only relatively recently that the area has been generally recognised as having undergone metamorphism at all.

Before the 1940's several workers noted the presence of phases or assemblages now considered diagnostic of low-grade metamorphism, although few realised their significance. One of the first descriptions



of a metamorphic assemblage was made by Woodland (1938) in the manganese beds of the Harlech Dome where he attributed the biotite, chlorite, sericite and garnet bearing assemblage to metamorphism within the chlorite zone of regional metamorphism. Pumpellyite was first positively identified in Wales by Nicholls (1959) within lower Ordovician spilites at Builth Wells, where it was thought to reflect metasomatism.

Jenkins and Ball (1964) identified pumpellyite within the soils of northern Snowdonia and identified the source as the basic intrusions of the area. Rast (1969) attributed the presence of prehnite and pumpellyite in the Welsh igneous rocks to low-grade zeolite facies metamorphism. Ridgeway (1971) described typical prehnite-pumpellyite and greenschist facies assemblages in the meta-dolerites of mid-Wales and attributed them to burial metamorphism with the higher grade greenschist facies assemblages reflecting a greater thickness of overburden. Floyd et al. (1976) described typical low-grade assemblages in the meta-dolerites of the Conwy Valley.

Prehnite and pumpellyite bearing assemblages in the basic rocks of the Fishguard Volcanic Group were recognised by Bevins (1978, 1979), and attributed by him to prehnite-pumpellyite facies metamorphism.

Roberts (1979) records the presence of widespread prehnite-pumpellyite and greenschist assemblages within the basic rocks of northern Snowdonia and from the disposition of these assemblages produced isograds for northern Snowdonia and Llyn (Roberts, 1981). Metamorphism was regarded as being syn- or immediately post-deformation and broad correlation between the grade of metamorphism and the intensity of deformation was recognised.

Bevins et al. (1981) described the low-grade metamorphism of the

Welsh basin utilising both meta-basic secondary mineral assemblages and illite crystallinity. Bevins and Rowbotham (1983) examined secondary mineral assemblages and phase compositions developed within the meta-dolerites of the Welsh basin and distinguished an area of generally higher grade (actinolite-bearing assemblages) in the central Welsh basin flanked by an area of generally lower grade (prehnite- and pumpellyite-bearing assemblages) towards the margins of the basin. Estimates of temperatures and pressures range from 325°C and 3.4 kb in the central part of the basin to 125°C and 1.3 kb at the margins of the basin.

## 1.5. Techniques employed

### 1.5.1. Field techniques

The major objective of the fieldwork was the collection of representative samples for detailed laboratory observation and analysis. Samples were taken from all lithologies but emphasis was initially placed on the meta-basic rocks (dolerites, basalts and basic tuffs). As the project developed numerous samples of argillaceous sediment and vein quartz were taken.

In addition to sample collection more specific fieldwork was undertaken concerning in particular: i) the relative age of the quartz veining, ii) the timing of dolerite emplacement relative to deformation, iii) internal variation within the dolerites in terms of grain size, fracturing, jointing etc., and, iv) the intensity and style of deformation.

These field observations assist in the interpretation of laboratory observations and results.

### 1.5.2. Laboratory techniques

Brief summaries of the techniques utilised in the project are outlined in the order in which they are discussed in the following chapters.

- i) Geochemistry - From the meta-dolerites of the Conwy Valley, 103 samples and 34 samples were analysed for major and trace elements respectively. This data allowed some quantification of the effects of metamorphism on the initial dolerite chemistry. In addition, the geochemistry provides a data base essential for the interpretation of the petrographic and phase chemistry results.
- ii) Petrography - Detailed thin section observations were made on 194 meta-dolerites taken throughout northern Snowdonia. Secondary mineral assemblages were recorded in order to quantify regional and local variation in secondary phases, degree of recrystallisation and the site of alteration were also recorded.
- iii) Phase chemistry - Electron microprobe analyses were obtained for phases in 16 meta-dolerites and 1 meta-diorite from the Conwy Valley. Interpretation of the phase chemistry results, in conjunction with the geochemical results, allows the relative influence of host rock composition and metamorphic parameters on secondary phase composition to be evaluated.
- iv) Illite crystallinity - 120 illite crystallinity determinations were performed on fine-grained sedimentary lithologies. Illite crystallinity enabled metamorphic characteristics to be determined in those areas and at specific stratigraphic levels where suitable meta-dolerites were absent.
- v) White mica  $b_0$  - 50 white mica  $b_0$  measurements were made on representative mudstone, shale and slate lithologies. These results provide information on the facies series of metamorphism, hence an indication of the relative pressure/temperature conditions.

- vi) Fluid inclusion analysis - Fluid inclusions in 19 vein quartz samples taken throughout northern Snowdonia were examined. Minimum trapping temperatures are obtained by heating the inclusions to homogenisation. Interpretation of homogenisation temperatures, with reference to independent geological data for either pressure or temperature allow an estimate of the parameter for which data is lacking.

## CHAPTER 2

### GEOCHEMISTRY OF THE META-DOLERITES

#### 2.1. Introduction

A large number of meta-dolerite intrusions occur throughout northern Snowdonia. Since these meta-dolerites display compositions suitable for the development of critical secondary phases and diagnostic mineral assemblages (Smith, 1968; Bevins, 1978; Bevins and Rowbotham, 1983, etc.,) they have been examined in some detail. The intensity of metamorphic recrystallisation is variable but has only rarely been pervasive enough to totally obliterate the primary igneous texture and mineralogy with the dolerites often displaying relict igneous clinopyroxene, magnetite and (rarely) labradoritic plagioclase. Characteristic secondary phases recognised in the Conwy Valley meta-dolerites include chlorite, albite, epidote, prehnite, pumpellyite, actinolite, quartz, calcite, sphene, stipnomelane and white mica. In this and the following two chapters meta-dolerite geochemistry, petrography and mineral compositions are examined respectively.

Under low-grade metamorphic conditions it has been shown that local changes in bulk rock chemistry can play an important role in controlling specific mineral development (Smith, 1968) and the precise chemical composition of secondary phases (Bishop, 1972; Bevins, 1979 and Oliver and Leggett, 1980). It has also been shown that progressive change in metamorphic conditions (temperature, pressure and fluid composition) are also reflected by systematic changes in mineral chemistry (Bishop, 1972; Liou et al., 1983). Hence it is clear that in order to interpret the petrographic observations and detailed mineral chemistry of chapters 3 and 4 the geochemical characteristics of the meta-dolerites

must first be examined in order to assess and quantify the degree of host rock compositional control.

During the course of the fieldwork a representative number of meta-dolerite samples were taken for bulk rock geochemical analysis. A total of 103 samples, taken from a number of the sills exposed throughout the Conwy Valley, were analysed for the major and minor elements  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$  and  $\text{H}_2\text{O}$ . In addition 34 samples from the large Moel Siabod intrusion were analysed for the trace elements Ce, Nd, La, Rb, Sr, Y, Zr, Hf, Ba, Ni and Cr.

The main aims of the geochemical determinations were:-

- i) to examine the relationship between bulk rock geochemistry, petrography and metamorphic phase composition in order to assess the importance of bulk rock major element geochemical control on the development of specific metamorphic phases and mineral assemblages and the relative compositions of the secondary minerals. In this respect the geochemical analyses provide a data base essential for the interpretation of both the petrographic observations and the results of the electron microprobe phase composition determinations.
- ii) to semi-quantitatively examine relative element mobility during low-grade metamorphism.
- iii) a brief investigation of the broad chemical affinities and primary magmatic characteristics of the intrusions as revealed by their general chemical characteristics and in particular the abundance and distribution of relatively immobile major and trace elements.
- iv) to examine the chemical variation apparent both within and between the individual meta-dolerite intrusions in terms of both the magmatic and post-magmatic processes.

FIGURE 2.1. A map of the Conwy Valley showing the distribution of meta-dolerite intrusions, from Roberts (1979).

## 2.2. Sample collection and preparation

Representative geochemical samples were taken from meta-dolerite sills throughout the Conwy Valley. For several intrusions a number of samples were taken in a traverse across an intrusion, in other cases this was not possible and only samples from within the main body of the intrusion were taken. Figure 2.1. is a map showing the distribution of meta-dolerites within the Conwy Valley and showing the location of the intrusions sampled. The precise locations of the individual geochemical samples are listed in Appendix 2 (i).

In the field, samples were chosen to provide representative cross-sections through the main intrusions (for example, Moel Siabod, Craig Wen and Tal-y-Fan), and to reflect any obvious variation in texture and mineralogy. Also a number of small, isolated intrusions were sampled including an unnamed intrusion north of Tal-y-Fan (SH 725728) and an intrusion on the south side of Cwm Eigiau. Samples of approximately 2kg. were taken with as much weathered material as possible removed. In general veined material, containing mainly epidote, calcite and quartz, was excluded although some fine veining was not readily seen in the hand specimens and had to be removed during splitting. As well as the large geochemical sample a small hand specimen was taken at each location for petrographic and possible microprobe examination.

Sample preparation consisted of initially splitting the sample into small blocks excluding, at this stage, any remaining weathered or veined material. The sample was further crushed in a Sturtevant jaw crusher before the amount of sample was reduced to approximately 200gm by cone and quartering. 50 and 120gm sub-samples were then terna-milled for 15 and 40 seconds respectively, the former for FeO determinations utilising standard wet chemical techniques, and the latter for X-ray fluorescence analysis. The larger sub-sample was homogenised and a 30gm portion ball-



milled for approximately 20 minutes. Fused discs were produced by mixing sample (previously ignited at  $1000^{\circ}\text{C}$ ) in a 1:5 ratio with ignited lithium metaborate flux, fusion being achieved by heating the sample/flux mixture to approximately  $1200^{\circ}\text{C}$  over a meker burner for 30 minutes. The fused liquid was then cast into a glass disc on a brass casting plate and pressed into shape with an aluminium plunger. The fused disc was then allowed to slowly cool. Pressed pellets were produced by mixing about 10 drops of Mowiol binder with 6gm of ball-milled sample. Pellets were cast in a tungsten carbide press at a pressure of 20 tons per square inch for 4 minutes. The pellets thus produced were then oven dried overnight. Most major element analyses were undertaken on the glass discs, whereas  $\text{Na}_2\text{O}$ , and trace element analyses were performed on the pressed powder pellets. Analysis was by standard X-ray fluorescence spectrometry.

A detailed account of the sample preparation techniques employed and an outline of the analytical procedures can be found in Daly (1978), Bevins (1979) or Haselock (1982). The machine conditions employed and an assessment of the accuracy and detection limits of the technique are presented in Appendix 1 (i). The results of the geochemical analyses for both major and trace elements are presented in Appendix 3 (i) and 3 (ii) respectively.

### 2.3. Bulk major element characteristics

In Table 2.A. the mean major and minor element geochemical characteristics of the Conwy Valley meta-dolerites are compared with those of average basalts (Manson, 1968) and average spilites (Vallance, 1969). It can clearly be seen that in many respects the Conwy Valley meta-dolerites display the chemical characteristics of fresh basalts, particularly in terms of  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$ . In addition the mean  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio

Oxide (wt %)	Average basalt (Manson, 1968)	Average spilite (Vallance, 1969)	Average Conwy Valley meta-dolerite
SiO <sub>2</sub>	49.2	49.0	47.0
TiO <sub>2</sub>	1.9	1.5	1.99
Al <sub>2</sub> O <sub>3</sub>	15.8	15.4	15.37
Fe <sub>2</sub> O <sub>3</sub>	3.0	4.1	2.78
FeO	8.0	6.1	7.93
MnO	0.17	0.18	0.21
MgO	6.6	5.3	8.06
CaO	10.0	7.6	9.38
Na <sub>2</sub> O	2.7	4.1	2.57
K <sub>2</sub> O	1.0	1.1	0.50
P <sub>2</sub> O <sub>5</sub>	0.33	0.3	0.28
H <sub>2</sub> O	0.9	3.2	4.23
Fe <sub>2</sub> O <sub>3</sub> /FeO	0.38	0.67	0.39
FeO*/MgO	1.62	1.85	1.53

TABLE 2.A. Comparison of mean element data for the Conwy Valley meta-dolerites with average basalt and average spilite.

Oxide (wt %)	Average basalt (Manson, 1968)	Average spilite (Vallance, 1969)	Average Conwy Valley meta-dolerite
SiO <sub>2</sub>	49.2	49.0	47.0
TiO <sub>2</sub>	1.9	1.5	1.99
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Fe <sub>2</sub> O <sub>3</sub>	3.0	4.1	2.78
FeO	8.0	6.1	7.93
MnO	0.17	0.18	0.21
MgO	6.6	5.3	8.06
CaO	10.0	7.6	9.38
Na <sub>2</sub> O	2.7	4.1	2.57
K <sub>2</sub> O	1.0	1.1	0.50
P <sub>2</sub> O <sub>5</sub>	0.33	0.3	0.28
H <sub>2</sub> O	0.9	3.2	4.23
Fe <sub>2</sub> O <sub>3</sub> /FeO	0.38	0.67	0.39
FeO*/MgO	1.62	1.85	1.53

TABLE 2.A. Comparison of mean element data for the Conwy Valley meta-dolerites with average basalt and average spilite.

FIGURE 2.2.  $H_2O$  vs  $Fe_2O_3/FeO$  for the meta-dolerites from the Conwy Valley, showing a mean basalt, a submarine weathering trend and a spilitisation trend, from Floyd and Tarney, (1979).

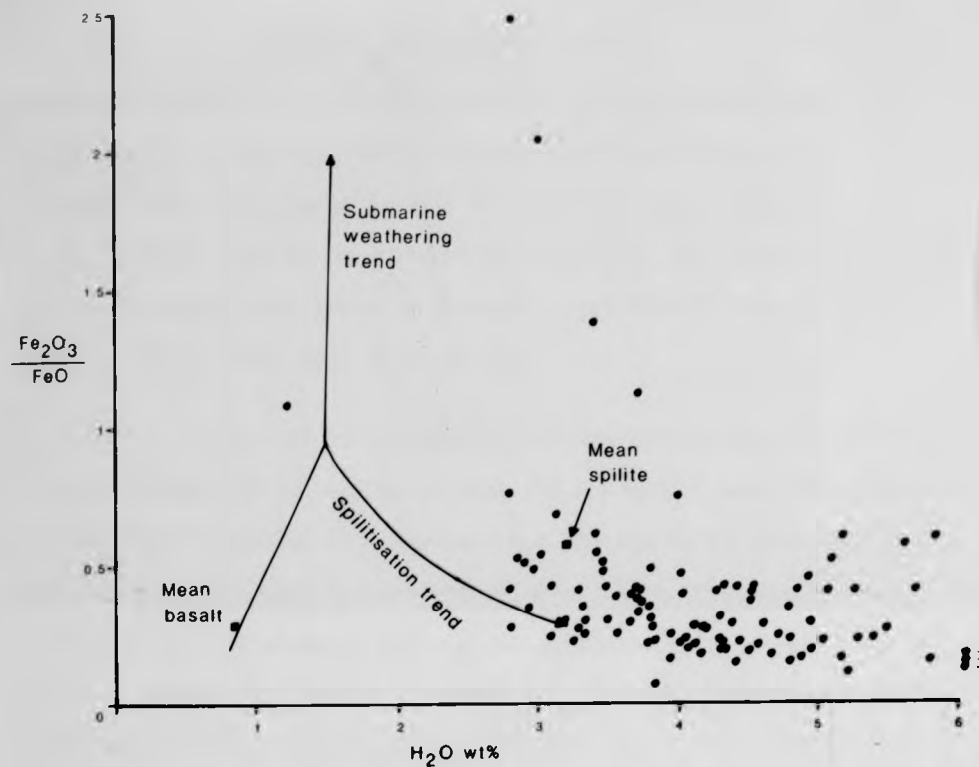
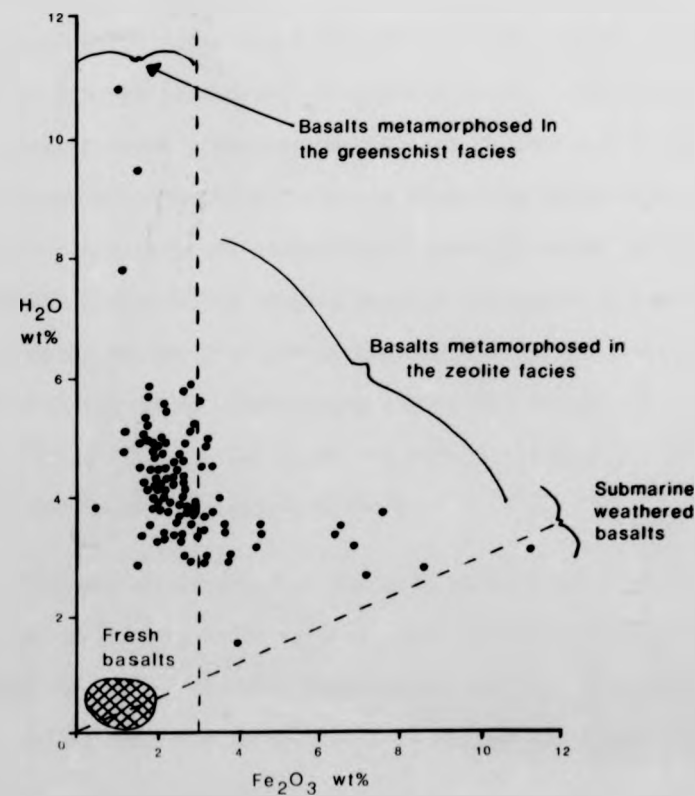


FIGURE 2.3.  $H_2O$  vs  $Fe_2O_3$  for the meta-dolerites from the Conwy Valley, showing the fields for fresh basalt, submarine weathered basalt, and basalts metamorphosed in the zeolite and the greenschist facies, from Miyashiro et al. (1971).



is comparable to that of fresh basalts. The mean  $\text{SiO}_2$  and  $\text{K}_2\text{O}$  values are both rather lower, and the mean  $\text{MgO}$  and  $\text{H}_2\text{O}$  values rather higher than either average basalts or average spilites. Obviously any comparison between mean bulk elemental data for different rock types can be of only limited value as no information concerning the range in composition observed within each group is conveyed, particularly for elements such as  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{H}_2\text{O}$ .

One feature that is immediately evident from a comparison of the data contained in Table 2.A. is that the intrusions have been subject to large scale hydration with the mean  $\text{H}_2\text{O}$  content being in excess of 4%, as compared to a mean  $\text{H}_2\text{O}$  content of about 1% in fresh basic rocks. Figure 2.2. is a plot of  $\text{H}_2\text{O}$  against oxidation ratio (after Floyd and Tarney, 1979), showing a low temperature alteration trend (submarine weathering) and a higher temperature alteration trend (spilitisation). Clearly the samples from the Conwy Valley fall, as might be expected, along the relatively high temperature alteration trend. Figure 2.3. plots  $\text{Fe}_2\text{O}_3$  against  $\text{H}_2\text{O}$  and has been used by Miyashiro et al. (1971) to differentiate between fresh submarine basalts and gabbros and those subjected to a range of alteration including submarine weathering, zeolite facies metamorphism and greenschist/amphibolite facies metamorphism. The majority of the Conwy Valley samples plot in the higher grade alteration field (73% of samples in the greenschist/amphibolite facies field with a smaller number plotting in the lower grade alteration fields (23% in the zeolite facies field, 4% along the submarine weathering trend). No samples plot in the fresh basalt/gabbro field.

From a preliminary examination of the bulk rock, major element geochemical characteristics, it is evident that the Conwy Valley dolerites have been subject to relatively high temperature, hydrous metamorphism. Hence, it is probable that the marked chemical variation observed within

the meta-dolerites reflects the effects of both primary magmatic variation and relative element mobility during later metamorphism. It is, therefore, necessary to assess and quantify the effects of both primary and secondary processes on meta-dolerite geochemistry within the Conwy Valley.

#### 2.4. Element mobility during metamorphism

##### 2.4.1. Introduction

In the present context it is important that relative element mobility within the meta-dolerites of the Conwy Valley is examined in order to assess: i) the petrographic observations of Chapter 3, particularly in terms of the relative abundance of the dominant secondary mineral phases, and ii) the degree to which the chemical variation is due to secondary processes. Approximate relative element mobility is examined by the use of inter-element correlation matrices which are presented in Tables 2.B., 2.C., and 2.D. This approach presents the data in a convenient form and enables a simple quantification of inter-element relationships. For the major element correlation matrix there is a problem in that some correlation must occur because of the effects of summation to 100%. The major drawback to this type of approach is that the results are not presented visually, to compensate for this some binary element plots are also presented to illustrate examples of specific geochemical features.

##### 2.4.2. The correlation matrices

Three correlation matrices are presented representing i) major elements (Table 2.B), ii) trace elements (Table 2.C), and iii) a combination of the more mobile trace and major elements (Table 2.D), the last Table being derived from the first two.

TABLE 2.B. Major element correlation matrix

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	FeO* MgO	Fe <sub>2</sub> O <sub>3</sub> FeO
SiO <sub>2</sub>	1.0													
TiO <sub>2</sub>	.01	1.0												
Al <sub>2</sub> O <sub>3</sub>	-.05	-.67	1.0											
Fe <sub>2</sub> O <sub>3</sub>	.01	.35	-.33	1.0										
FeO	-.01	.68	-.38	4.16	1.0									
MnO	-.08	.72	-.66	.25	.59	1.0								
MgO	-.53	-.58	.18	-.40	-.27	-.35	1.0							
CaO	-.25	-.19	.01	.31	-.56	-.29	.11	1.0						
Na <sub>2</sub> O	.70	.34	-.13	.12	.18	-.23	-.70	-.30	1.0					
K <sub>2</sub> O	.14	.11	.14	-.01	.06	.08	-.22	-.19	-.02	1.0				
P <sub>2</sub> O <sub>5</sub>	.25	.62	-.42	.30	.47	.43	-.59	-.33	.28	.22	1.0			
H <sub>2</sub> O	1.60	.23	.13	1.43	.16	.08	1.66	-.28	1.60	-.22	-.21	1.0		
FeO*	-.11	.86	-.70	4.47	4.68	.78	-.47	-.26	.21	.00	.61	-.12	1.0	
FeO*/ MgO	.04	2.88	-.39	4.64	4.24	.41	4.75	-.12	3.51	.13	4.77	-.42	3.48	1.0
Fe <sub>2</sub> O <sub>3</sub> / FeO	.09	.02	-.05	4.84	4.48	-.07	-.30	-.49	.01	-.04	.09	-.33	.08	.59

KEY: 1 - 3 high H<sub>2</sub>O values removed; 2 - for samples with FeO\*/MgO < 2.2; 3 - with single very high FeO\*/MgO value removed.

4 - Possible auto correlation.

From the literature the major elements  $TiO_2$  and  $P_2O_5$  are considered essentially immobile during low-grade metamorphism (Winchester and Floyd, 1976) as is the  $FeO^*/MgO$  ratio (Miyashiro et al., 1971; Vallance, 1974);  $MgO$ ,  $Al_2O_3$  and  $FeO^*$  (total iron as  $FeO$ ) are considered slightly mobile during low-grade metamorphism (Vallance, 1965); whilst  $SiO_2$ ,  $CaO$ ,  $K_2O$ ,  $Na_2O$  and  $H_2O$  are considered highly mobile during low-grade metamorphism (Vallance, 1965; Humphris and Thompson, 1978). Table 2.B. clearly indicates that this general pattern is applicable to the Conwy Valley meta-dolerites.  $TiO_2$  and  $P_2O_5$  display relatively good correlation with  $Al_2O_3$ ,  $MnO$ ,  $FeO$ ,  $FeO^*$ ,  $MgO$  and the  $FeO^*/MgO$  ratio. Correlation between  $TiO_2$  and  $FeO^*$  and the  $FeO^*/MgO$  ratio is particularly good ( $r = > .86$ ), perhaps indicating that although the oxidation state of iron is variable, total iron and the  $FeO^*/MgO$  ratio remain relatively constant throughout low-grade metamorphism. Of the more commonly mobile components within the matrix several interesting correlations exist, for example, good negative correlation ( $r = > - .5$ ) exists between  $SiO_2 - MgO$ ,  $Na_2O - MgO$ ,  $SiO_2 - H_2O$  and  $H_2O - Na_2O$ , whilst good positive correlation ( $r = > .65$ ) exists between  $SiO_2 - Na_2O$  and  $MgO - H_2O$ . The correlations are thought to reflect specific mineralogical and petrographic trends and are discussed in more detail in the next Chapter.

Trace elements were analysed for in the 34 samples collected from the Moel Siabod intrusion. From the literature the trace elements Zr, Y and Nb generally remain immobile during low-grade metamorphism (Cann, 1970; Winchester and Floyd, 1976) whilst Rb, Sr and Ba are generally mobilised (Cann, 1970; Pearce and Cann, 1973). From Table 2.C. it can be seen that good positive correlation ( $r = > .88$ ) exists between Zr, Nb and Y supporting the view that they have remained immobile during low-grade metamorphism. In addition, good correlation ( $r = > .82$ ) exists



TABLE 2.C. Trace element correlation matrix

	Ce	Nd	La	Rb	Sr	Y	Zr	Nb	Ba	Ni	Cr	Nb Y	Zr P <sub>2</sub> O <sub>5</sub>	FeO* MgO	H <sub>2</sub> O
Ce	1.0														
Nd	.85	1.0													
La	.93	.82	1.0												
Rb	.46	.53	.46	1.0											
Sr	.10	.06	.3	.54	.22	1.0									
Y	.93	.85	.94	.48	.21	1.0									
Zr	.92	.84	.95	.44	.44	.96	1.0								
Nb	.86	.82	.87	.37	.08	.88	.89	1.0							
Ba	.02	.07	.3	.21	.76	.32	.12	.08	.03	1.0					
Ni	-.52	-.31	-.43	-.16	-.06	-.60	-.59	-.43	-.13	1.0					
Cr	-.66	-.58	-.60	-.28	-.20	-.66	-.63	-.58	-.01	.72	1.0				
Nb Y	-.40	-.03	-.43	-.19	-.21	.5	.45	-.39	-.19	.43	.42	1.0			
Zr P <sub>2</sub> O <sub>5</sub>	.64	.49	.69	.18	.32	.72	.5	.75	.62	.04	-.49	-.49	1.0		
FeO* MgO	2.85	2.80	.85	2.49	2.21	.83	.87	2.84	.04	-.60	-.55	-.30	.73	1.0	
H <sub>2</sub> O	-.15	-.03	1.33	-.21	1.57	1.38	1.26	-.26	-.32	1.40	1.39	1.49	1.50	1.40	1.0

KEY: 1 - 3 high H<sub>2</sub>O values removed; 2 - one high FeO\*/MgO value removed; 3 - 3 high La values removed;  
 4 - 3 high Zr values removed, 5 - possible auto correlation.

between these elements and La, Ce and Nd, suggesting that these elements also have remained essentially immobile throughout low-grade metamorphism. In contrast, poor correlation ( $r = < .5$ ) exists between these immobile elements and Rb, Sr and Ba, supporting the view that these later elements were mobilised. However, good correlation ( $r = .76$ ) exists between Rb and Ba, a reflection that these trace elements are closely associated, particularly within the crystal structure of the feldspars. Correlation between the immobile elements and Ni and Cr is negative and rather poor ( $r = < - .65$ ), a reflection that the incompatible trace elements are concentrated in magmatic differentiates whilst compatible Ni and Cr are readily removed from the magma during the crystallisation of olivine and pyroxene. In addition, some mobilisation of these elements might have occurred during alteration (Pearce and Cann, 1973) with Ni in particular being concentrated in olivine and, therefore, being subject to mobilisation as olivine breaks down. Low-grade metamorphism could cause significant variation in the Ni and Cr values thus accounting for their relatively poor correlation with the immobile trace elements.

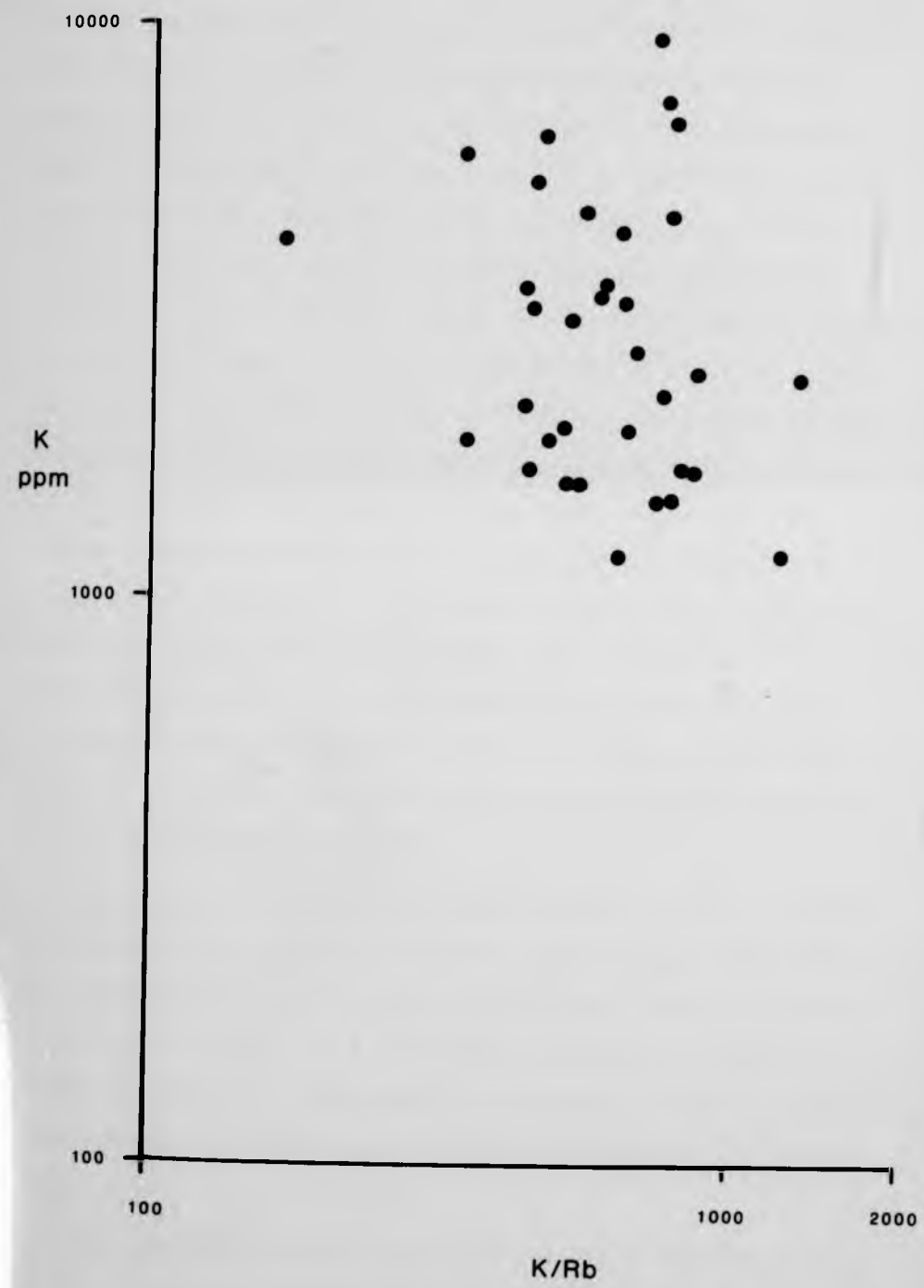
Correlation between the  $\text{FeO}^*/\text{MgO}$  ratio and the immobile elements is also relatively good ( $r > .80$ ) indicating that this ratio can be reliably used as a measure of differentiation even after low-grade metamorphism (Floyd, 1983). Table 2.D. is a correlation matrix for the relatively mobile major and trace elements  $\text{SiO}_2$ , CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{H}_2\text{O}$ , Rb, Sr and Ba. The correlation between  $\text{Na}_2\text{O} - \text{SiO}_2$  and Ba - Rb has already been noted. Of the remaining elements good correlations exist between Sr - CaO, K - Rb and K - Ba. These correlations reflect the incorporation of a trace element associated with a specific major element into the crystal structure of a common mineral (Cann, 1970). The consistent negative correlation between  $\text{H}_2\text{O}$  and the other elements of Table 2.D. reflects the solubility and subsequent removal of these

TABLE 2.D. Correlation matrix for the more mobile elements

	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Sr	Rb	Ba	H <sub>2</sub> O
SiO <sub>2</sub>	1.0							
CaO	-.23	1.0						
Na <sub>2</sub> O	.59	-.40	1.0					
K <sub>2</sub> O	.36	.04	.17	1.0				
Sr	.21	.49	-.09	.36	1.0			
Rb	.45	-.27	.32	.84	.24	1.0		
Ba	.34	-.02	.35	.68	.33	.70	1.0	
H <sub>2</sub> O	1	-.40	-.43	-.35	1	-.22	-.34	1.0

Key  
 1 - 3 high H<sub>2</sub>O  
 values removed.

FIGURE 2.4. K vs K/Rb for the meta-dolerites from Moel Siabod.



elements in the presence of an aqueous fluid during low-grade metamorphism.

The very good correlation between  $K_2O$  and Rb ( $r = .84$ ) in the Moel Siabod intrusion indicates that although these elements have been mobile (Tables 2.B. and 2.C.), in relation to each other they would appear to have behaved as an essentially coherent element pair. As a result, even though the absolute values of K and Rb have little meaning, the K/Rb ratio might reflect the original K/Rb ratio of the fresh dolerites. However, when the K and Rb data from Moel Siabod are plotted on a K vs K/Rb diagram (Figure 2.4.) the effects of alteration can be readily seen. Hart (1969) and Hart and Nalwalk (1970) demonstrate that fresh basalts display a constant K/Rb ratio with variable K content. Alteration results in variable K vs K/Rb trends. Figure 2.4. clearly displays a broad scatter of data indicating that the observed distribution is related more to the effects of alteration than primary igneous processes. Floyd et al. (1976) describe a similar K vs K/Rb distribution with a broadly negative K vs K/Rb trend being related to alteration. Only the Pen-y-Gadair, Tal-y-Fan and Craig Eigiaw meta-dolerites were found, by Floyd et al. (1976), to display constant K vs K/Rb associated with relatively fresh basic rocks.

The relative effects of primary and secondary processes on element distribution can be examined through inter-element binary plots between i) an essentially immobile differentiation index, such as the  $FeO^*/MgO$  ratio, and, ii) water. Examples of these relationships are shown in Figures 2.5. and 2.6. where examples of relatively more and less mobile major elements are plotted against the  $FeO^*/MgO$  ratio and  $H_2O$  respectively.

The correlation matrices suggest that on the hand specimen scale:-  
i)  $TiO_2$ ,  $P_2O_5$ , MnO, FeO,  $FeO^*$ , Ce, Nd, La, Y, Zr and Nb have remained essentially immobile.

FIGURE 2.5. The relationship between the  $\text{FeO}^*/\text{MgO}$  ratio and the relatively more and less mobile elements.

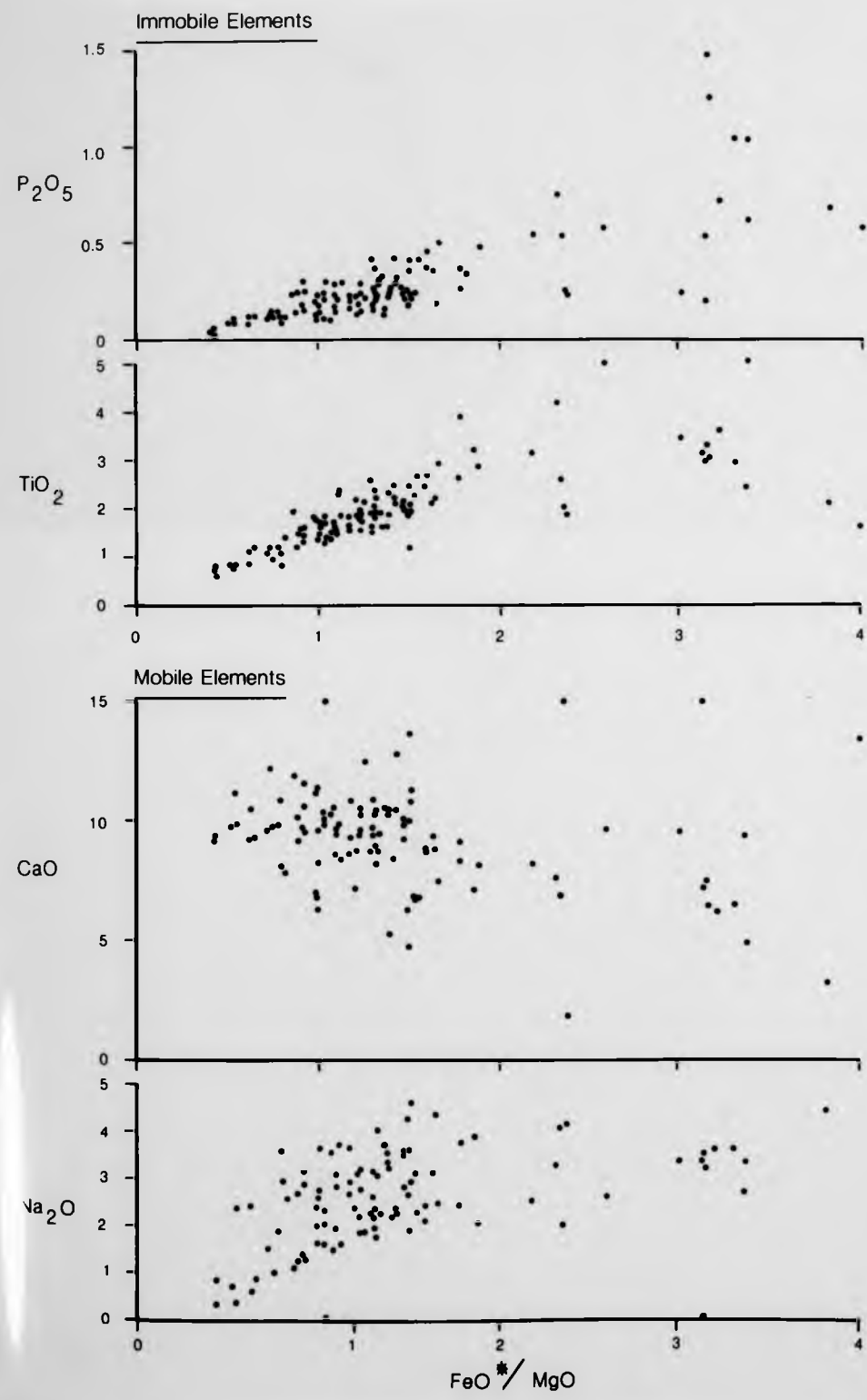
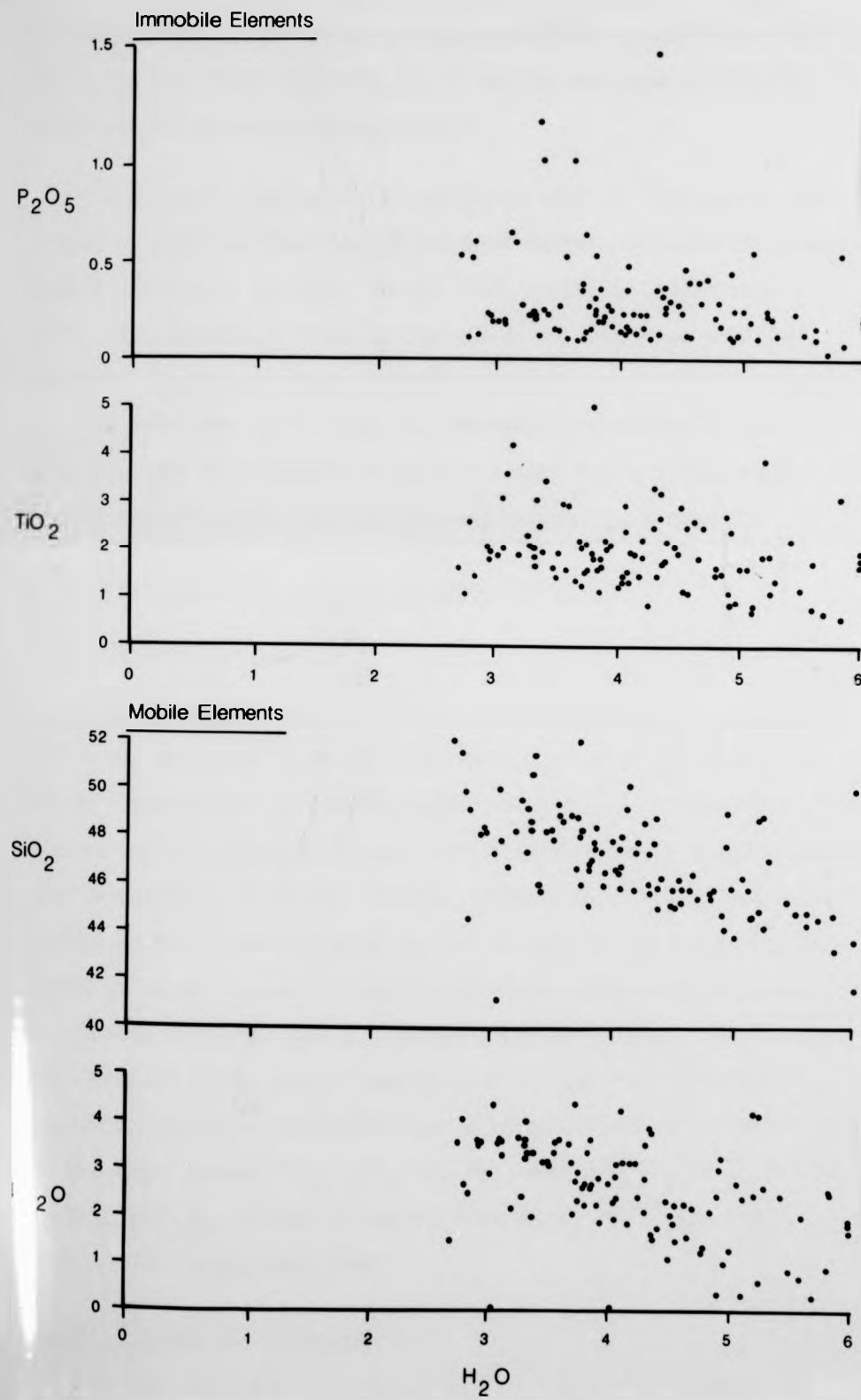


FIGURE 2.6. The relationship between  $H_2O$  and the relatively more and less mobile elements.



- ii)  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Ni}$  and  $\text{Cr}$  have been partially mobilised and,
- iii)  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{Rb}$ ,  $\text{Sr}$  and  $\text{Ba}$  have been extensively mobilised during low-grade metamorphism.

These results are generally consistent with the findings of other studies in areas of low-grade (greenschist facies) metamorphism (Cann, 1969; Miyashiro et al., 1971; Pearce, 1976; Humphris and Thompson, 1978). As a result of these conclusions it is clear that only the relatively less mobile major and trace elements can be confidently used to distinguish the primary magmatic geochemical characteristics of the meta-dolerites as variation in any of the more mobile elements may well reflect the effects of both magmatic and metamorphic processes.

## 2.5. Primary magmatic geochemical characteristics

### 2.5.1. Introduction

The effects of metamorphism on dolerite geochemistry in the Conwy Valley was discussed in Section 2.4. where a group of relatively less mobile elements was also distinguished. Variation in these elements or element ratios, therefore, should reflect differences in magmatic, rather than metamorphic, processes. Primary magmatic dolerite variation could reflect either a variable magma source, leading to the presence of a series of parent magmas of slightly different composition, or variation in magmatic processes such as fractional crystallisation. The elements and elemental ratios most frequently used for the study of primary magmatic geochemical characteristics in rocks subject to low-grade metamorphism include  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{FeO}^*/\text{MgO}$ ,  $\text{Nb}$ ,  $\text{Zr}$ ,  $\text{Y}$ ,  $\text{Ni}$ ,  $\text{Cr}$ ,  $\text{Zr}/\text{TiO}_2$ ,  $\text{Zr}/\text{P}_2\text{O}_5$  and  $\text{Nb}/\text{Y}$  (Floyd and Winchester, 1975; Pearce and Norry, 1979; Floyd, 1983; etc).

### 2.5.2. Geochemical affinities

The bulk rock data are plotted on a triangular AFM diagram



FIGURE 2.7. AFM (A = Na<sub>2</sub>O + K<sub>2</sub>O, F = total Fe as Fe<sub>2</sub>O<sub>3</sub>, M = MgO) diagram for the meta-dolerites from the Conwy Valley.

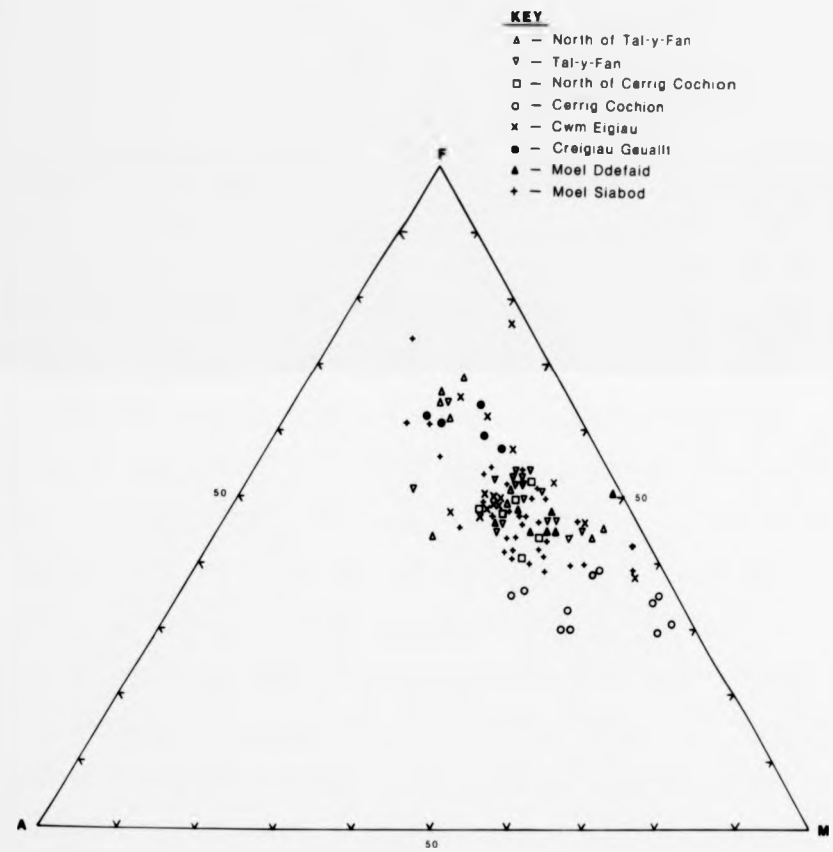
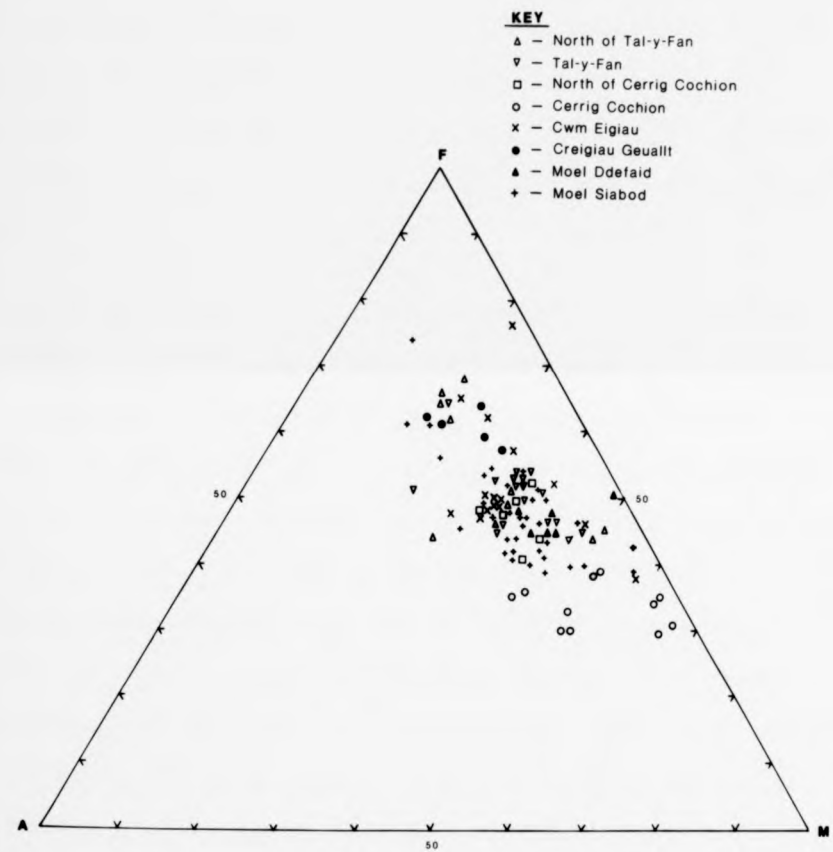


FIGURE 2.7. AFM (A = Na<sub>2</sub>O + K<sub>2</sub>O, F = total Fe as Fe<sub>2</sub>O<sub>3</sub>, M = MgO) diagram for the meta-dolerites from the Conwy Valley.



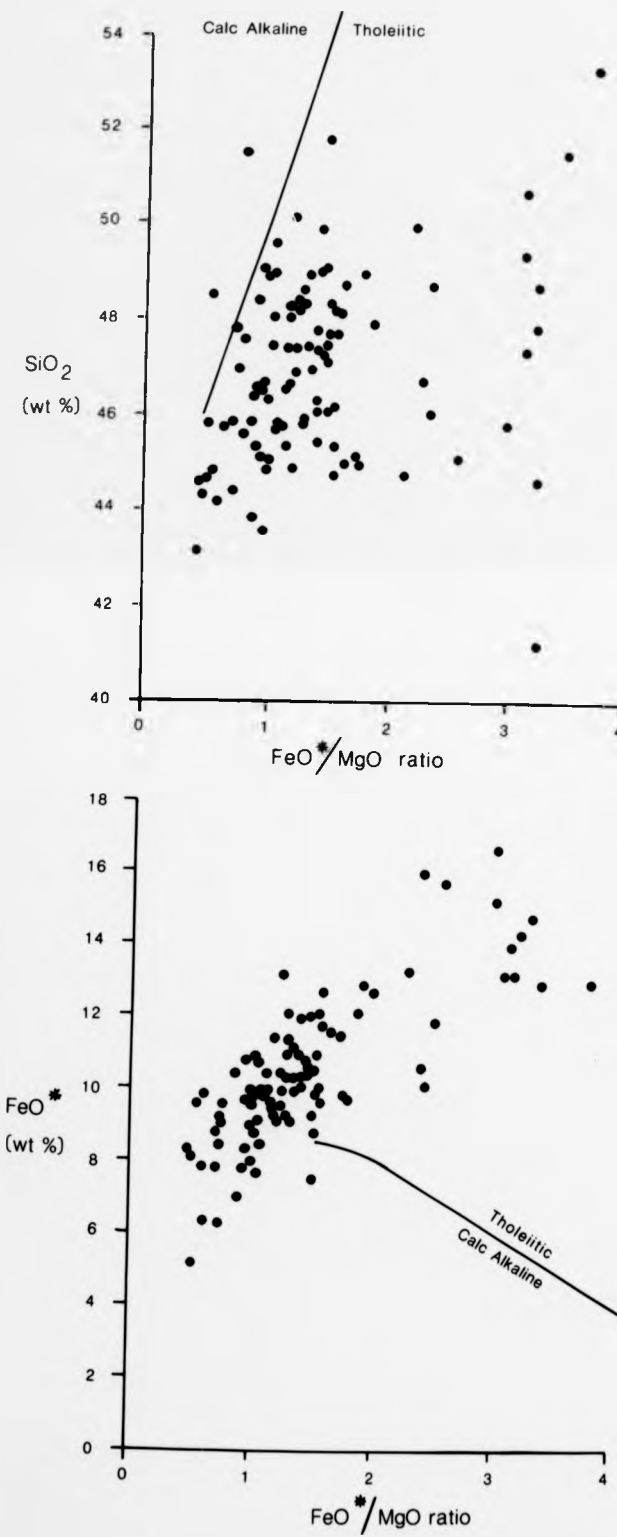
(Figure 2.7.) although this diagram is only of value if the elements used in its construction are known to have been essentially immobile during low-grade metamorphism, or if the effects of any alteration are known. In Section 2.4. it was shown that  $\text{FeO}^*$  and, to a lesser extent,  $\text{MgO}$  have remained relatively stable during low-grade metamorphism, whereas  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  appear to have been rather more mobile. The relative mobilisation of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  is responsible for the relatively broad scatter in the proportion of these alkali elements within the AFM diagram.

Despite the obvious effect of the mobilisation of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , the AFM diagram provides useful information concerning the relative amount of magmatic differentiation, and the distribution of points parallel to the F-M axis of the diagram suggests some degree of iron enrichment. The approximate degree of iron enrichment can be crudely quantified using the ratio  $\text{FeO}^*/\text{MgO}$  thereby producing a simple but useful measure of differentiation (Cox et al. 1979; Floyd, 1983). The  $\text{FeO}^*/\text{MgO}$  ratio increases progressively as relatively Mg rich phases such as olivine and clinopyroxene are precipitated. When iron-titanium oxides such as magnetite are precipitated the  $\text{FeO}^*/\text{MgO}$  ratio quickly falls as these minerals readily incorporate the excess iron. Alkali elements become progressively enriched in the later differentiates.

The distinct trend towards Fe enrichment, relative to Mg, in basic rocks is often strongly developed in tholeiitic rocks, moderately developed in alkaline rocks and only poorly developed in calc-alkaline rocks (Cox et al., 1979). The geochemical relationships observed in Figure 2.7. would, therefore, suggest that the meta-dolerites from the Conwy Valley represent variably differentiated intrusions that are probably tholeiitic in nature.

In Figure 2.8. the data from the Conwy Valley meta-dolerites are

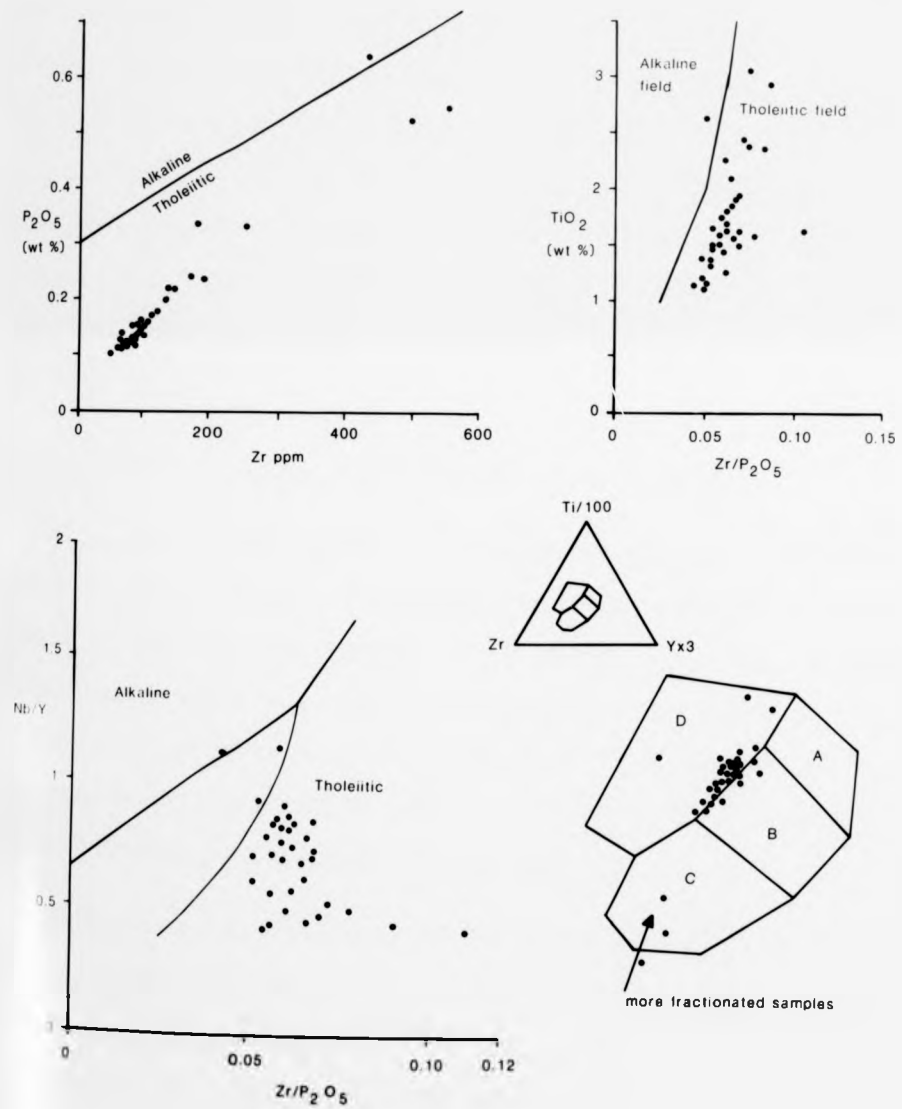
FIGURE 2.8.  $\text{FeO}^*/\text{MgO}$  vs  $\text{SiO}_2$  and  $\text{FeO}^*/\text{MgO}$  vs  $\text{FeO}^*$  for the Conwy Valley meta-dolerites showing the tholeiite and calc-alkaline compositional fields, from Miyashiro, 1974.



plotted on the  $\text{FeO}^*/\text{MgO}$  vs  $\text{SiO}_2$  and  $\text{FeO}^*/\text{MgO}$  vs  $\text{FeO}^*$  diagrams of Miyashiro (1974), which he used to distinguish tholeiite and calc-alkaline igneous suites. On the  $\text{FeO}^*/\text{MgO}$  vs  $\text{SiO}_2$  plot the data falls clearly in the tholeiite field with only 2 samples from Cerrig Cochion falling in the calc-alkaline field. On the  $\text{FeO}^*/\text{MgO}$  vs  $\text{FeO}^*$  plot the data straddles the calc-alkaline/tholeiite divide of Miyashiro. However, the trend developed clearly reveals  $\text{FeO}^*$  enrichment with increasing  $\text{FeO}^*/\text{MgO}$  (differentiation) which is typical of tholeiitic igneous suites. Miyashiro (1974) states that the exact position of the calc-alkaline/tholeiite divide is less significant than the response of  $\text{FeO}^*$  to increase in  $\text{FeO}^*/\text{MgO}$  with tholeiitic suites displaying relative iron enrichment and calc-alkaline suites relative iron depletion. By this criterion the Conwy Valley meta-dolerites display characteristics comparable with tholeiitic igneous suites.

A large number of magmatic discrimination diagrams have been proposed utilising trace elements, or a combination of trace and major elements (for example, Pearce and Cann, 1973; Floyd and Winchester, 1975; Pearce, 1975, etc.). For rocks affected by low-grade metamorphism only elements that are relatively stable during post consolidation processes are of value as their concentrations and/or element ratios should remain approximately constant. Elements and element ratios most widely used in this context include  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , Zr, Y, Nb,  $\text{Zr}/\text{P}_2\text{O}_5$  and Nb/Y (Floyd and Winchester, 1975; Winchester and Floyd, 1976). The discrimination diagrams of Figure 2.9. plot  $\text{P}_2\text{O}_5$  against Zr,  $\text{TiO}_2$  against  $\text{Zr}/\text{P}_2\text{O}_5$  and Nb/Y against  $\text{Zr}/\text{P}_2\text{O}_5$  respectively, and are taken from Floyd and Winchester (1975). In all three diagrams a majority of the Moel Siabod samples plot unequivocally within the tholeiitic or sub-alkaline fields with only one or two of the most differentiated samples (those with high  $\text{FeO}^*/\text{MgO}$  ratios) plotting close to the

FIGURE 2.9. Magmatic discrimination diagrams for the Moel Siabod meta-dolerite, i)  $P_2O_5$  vs Zr, ii)  $TiO_2$  vs  $Zr/P_2O_5$ , and iii)  $Nb/Y$  vs  $Zr/P_2O_5$ , showing the tholeiitic and alkaline compositional fields, from Floyd and Winchester (1975), and iv) the Ti-Y-Zr diagram showing the compositional fields of A Low-K tholeiites, B ocean floor basalts, C Calc-alkali basalts, and D Within-plate basalts, from Pearce and Cann (1973).



tholeiite/alkaline divide. The trace element evidence, therefore, would support the suggestion that the Moel Siabod meta-dolerite is an altered tholeiitic sill.

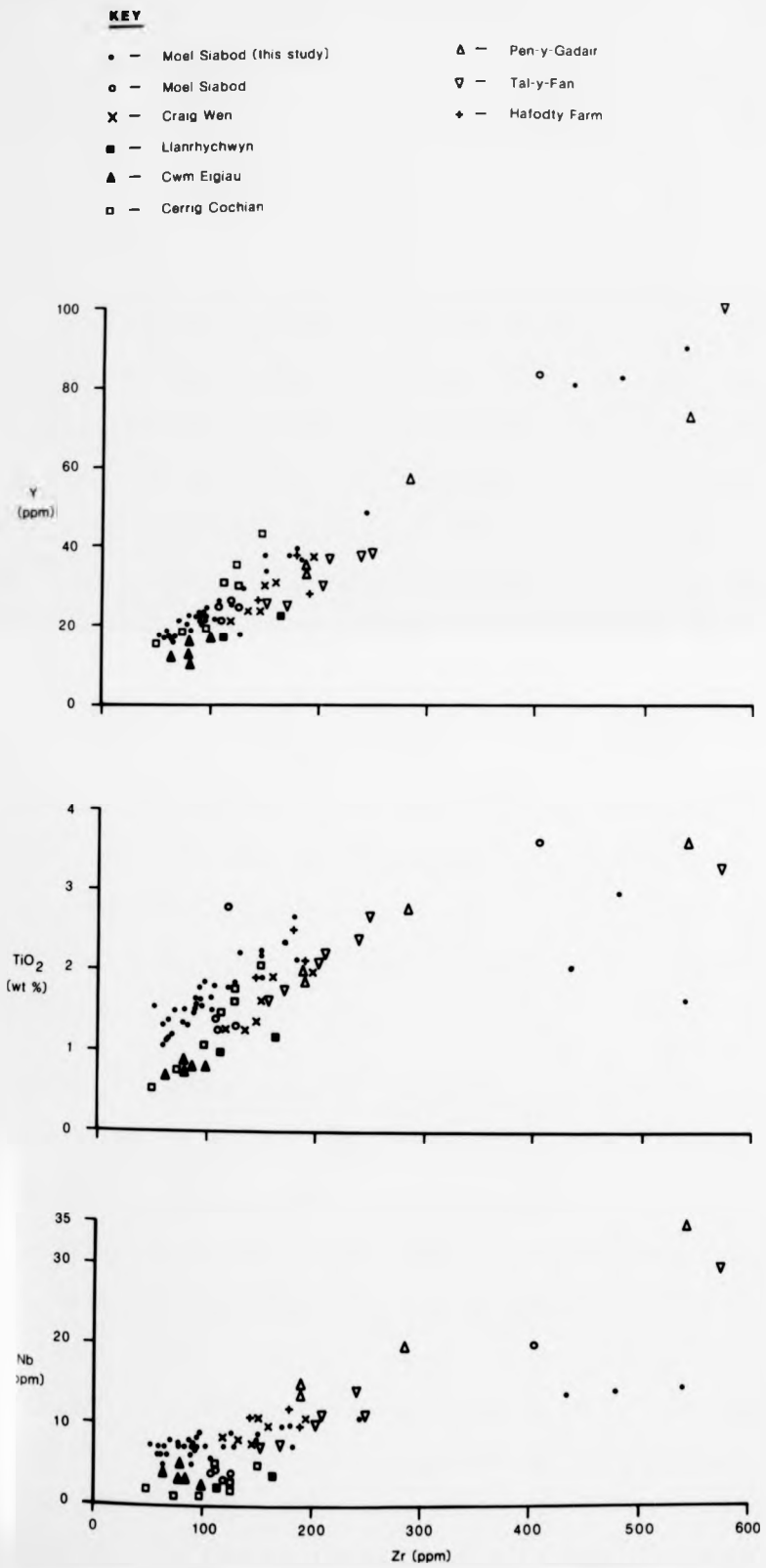
Finally, in Figure 2.9. the Moel Siabod samples are plotted on the triangular tectonic discrimination diagram of Pearce and Cann (1973). It is readily apparent that a majority of the samples plot in the field of 'within plate basalts' although some straddle the boundary into the field of 'typical ocean floor basalts'. The three pegmatitic, highly differentiated samples (169R1, 169R2 and 179C) plot within, or close to, the field of 'calc-alkaline basalts'. Floyd et al. (1976) described a similar distribution of results for meta-dolerites from the Conwy Valley.

#### 2.5.3. Primary variation in geochemical characteristics

A relatively large amount of primary geochemical variation exists within the meta-dolerites of the Conwy Valley that does not reflect the effects of low-grade metamorphism. It is possible for primary magmatic differences to occur as a result of differences in the degree or type of the fractionation process or the degree of initial partial melting resulting in the production of a series of parent magmas displaying subtly different geochemical characteristics.

If the tholeiitic intrusions of the Conwy Valley are derived from slightly different parent magmas, some evidence for this should exist in their incompatible element geochemistry (elements that do not readily enter common mineral phases). In the present study trace elements were only determined in the samples from Moel Siabod, however, some indication of the broader incompatible element geochemical trends within the Conwy Valley can be gained from the use of the geochemical data of Floyd et al. (1976) in conjunction with that obtained in the

FIGURE 2.10. Y vs Zr,  $TiO_2$  vs Zr and Nb vs Zr for a number of Conwy Valley meta-dolerite intrusions. Data from the present study and Floyd et al. (1976).





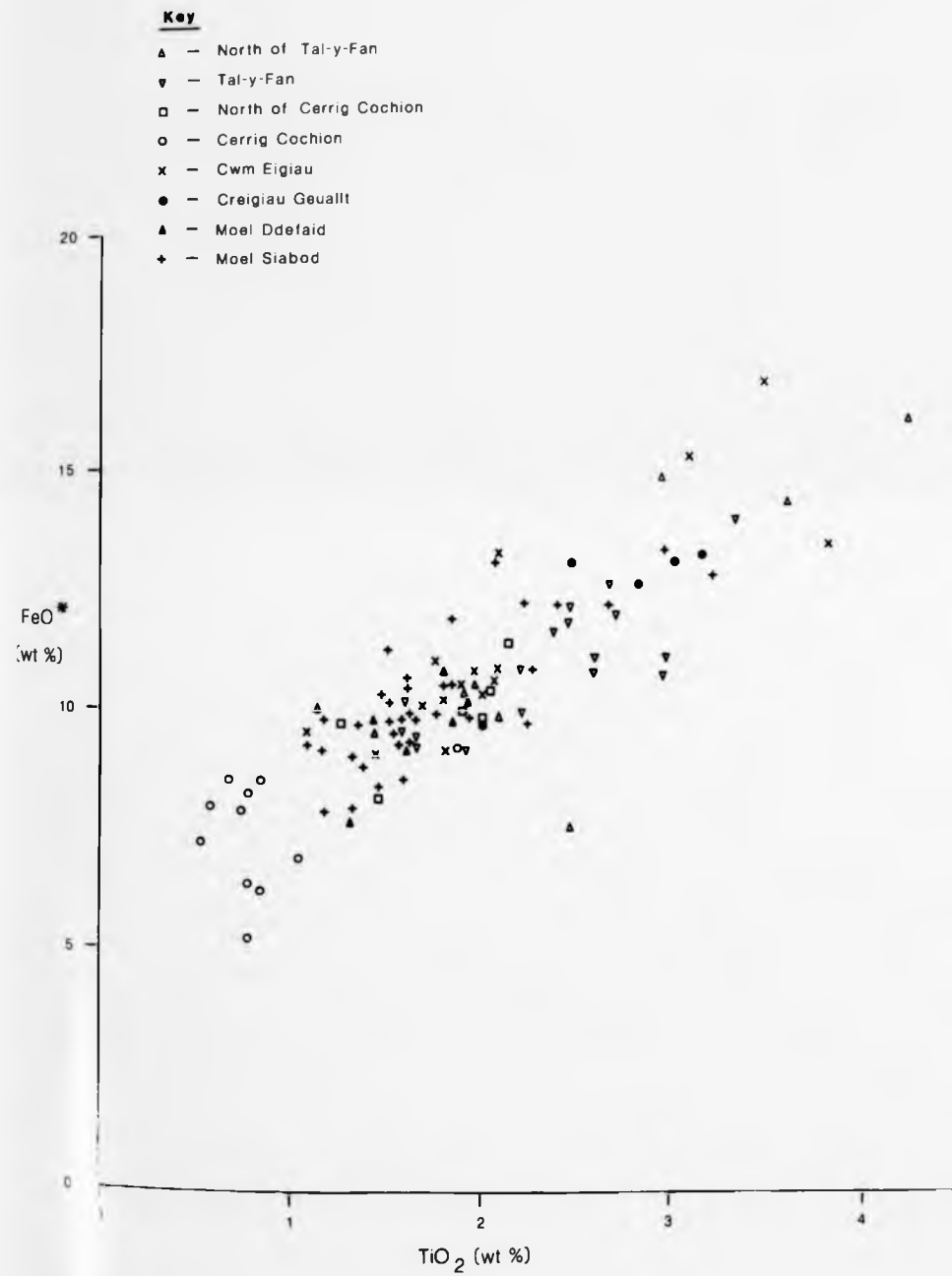
present study. In Figure 2.10.  $\text{TiO}_2$ , Y and Nb are plotted against Zr for a number of intrusions within the Conwy Valley. No systematic relationship exists between incompatible trace element distributions from different intrusions with intra-intrusion variation being as marked as inter-intrusion variation. Similarly if  $\text{FeO}^*$  is plotted against  $\text{TiO}_2$  (Figure 2.11) little variation exists in the relative distribution of  $\text{TiO}_2$  and  $\text{FeO}^*$  between intrusions with the overall data generally showing good positive inter-element correlation ( $r = .86$ ) with little spread. Floyd et al. (1976) recognised some variation in incompatible element ratios ( $\text{Nb/Y}$  and  $\text{Zr/P}_{205}$ ) with samples from the Cerrig Cochion, Craig Eigiau and Moel Siabod intrusions having generally lower  $\text{Nb/Y}$  and higher  $\text{Zr/P}_{205}$  than samples from other intrusions in the Conwy Valley.

As a result of the above observations it would appear that some primary variation in incompatible element geochemistry, particularly element ratios, can be recognised. However, this variation is not systematic leading to the conclusion that much of the variation in geochemistry between the dolerite sills of the Conwy Valley must reflect factors other than differences in the composition of the parent magma from which the dolerites are derived.

The nature and influence of fractionation processes on primary geochemistry can be investigated through the use of:-

i) an index of differentiation plotted against the compatible trace elements (those that readily enter common mineral phases), ii) compatible element binary relationships, and, iii) incompatible element binary relationships. A convenient major element differentiation index that has been used for low-grade meta-basic rocks is the  $\text{FeO}^*/\text{MgO}$  ratio (for example, Floyd, 1983). In Sections 2.4. and 2.5.2. it was shown that this ratio is little affected during low-grade metamorphism indicating that it probably accurately reflects primary differentiation

FIGURE 2.11. FeO\* (total iron as FeO) vs TiO<sub>2</sub> for the meta-dolerite intrusions of the Conwy Valley.

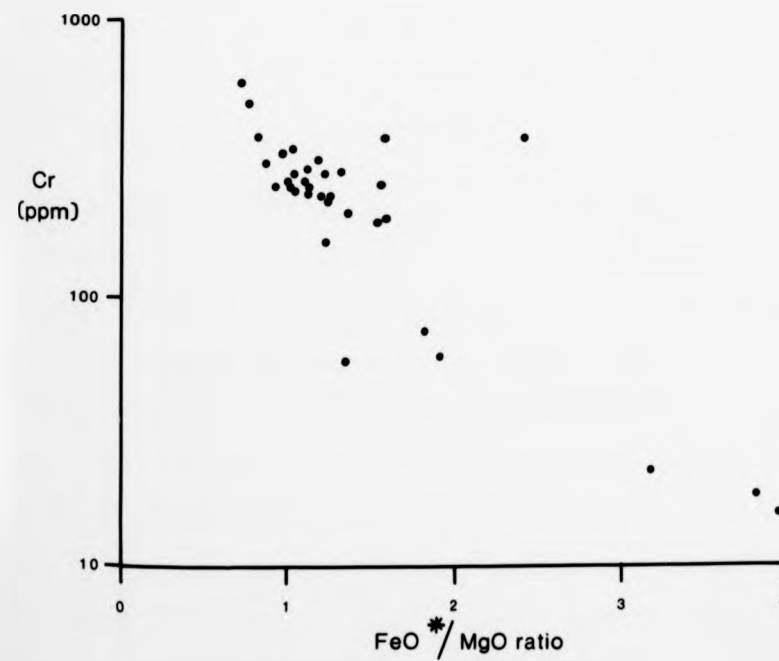
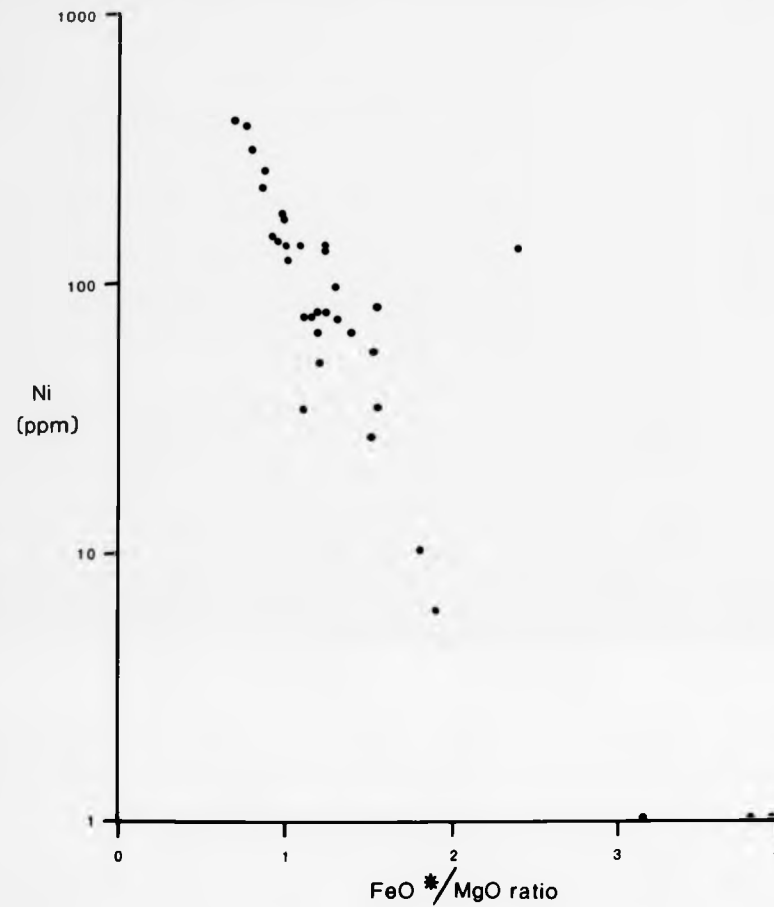


within the dolerites. The validity of this assumption can be tested by comparing the  $\text{FeO}^*/\text{MgO}$  ratio with other immobile element measures of differentiation.

Floyd et al. (1976) used the  $\text{Zr}/\text{TiO}_2$  ratio as a differentiation index in the meta-dolerites of the Conwy Valley. They observed that most meta-dolerites had  $\text{Zr}/\text{TiO}_2$  ratios of less than 0.010, a value indicative of little differentiated basalts. Several samples displayed significantly higher  $\text{Zr}/\text{TiO}_2$  ratios indicating significant differentiation. In the current project samples from Moel Siabod similarly display low  $\text{Zr}/\text{TiO}_2$  ratios with a mean  $\text{Zr}/\text{TiO}_2$  ratio of 0.006 (standard deviation = 0.0009), based on 31 samples. However much higher  $\text{Zr}/\text{TiO}_2$  ratios of 0.0334, 0.0163 and 0.0213 are displayed by the pegmatitic samples 169R1, 169R2 and 179C, respectively. This indicates that the pegmatitic vein from which samples 169R1 and 169R2 were taken and the very coarse grained, obviously discordant exposures around SH 555728, from which sample 179C was taken, represent highly fractionated portions of the main Moel Siabod intrusion. This view is further supported by the marked concentration of incompatible trace elements within these samples. Comparison of the  $\text{Zr}/\text{TiO}_2$  ratio with the  $\text{FeO}^*/\text{MgO}$  ratio reveals broad correlation with most of the Moel Siabod samples displaying  $\text{FeO}^*/\text{MgO}$  ratios of less than 2.0 but with the more differentiated samples 169R1, 169R2 and 179C having significantly higher  $\text{FeO}^*/\text{MgO}$  ratios of 7.25, 3.16 and 3.82 respectively.

In basic rocks the concentration of  $\text{TiO}_2$  progressively increases until fractionation of a Ti bearing ore phase.  $\text{TiO}_2$  is immobile during low-grade metamorphism so that a good correlation should exist between  $\text{TiO}_2$  and  $\text{FeO}^*/\text{MgO}$ . From Table 2.B. it is clear that good correlation ( $r = .88$ ) exists between  $\text{TiO}_2$  and  $\text{FeO}^*/\text{MgO}$  in samples with  $\text{FeO}^*/\text{MgO}$  ratios of less than 2.2. The relatively poor correlation in the more

FIGURE 2.12. Ni vs the FeO\*/MgO ratio and Cr vs the FeO\*/MgO ratio for the Moel Siabod meta-dolerite.



differentiated samples probably reflects the removal of  $TiO_2$  during later fractionation.

In Figure 2.12. Ni and Cr are plotted against the  $FeO^*/MgO$  ratio. Both plots reveal a sharp decline in compatible element with increase in  $FeO^*/MgO$ , reflecting the fractionation of olivine, clinopyroxene and/or magnetite (Floyd, 1983). Scatter within these plots probably reflects later mobilisation of Cr and particularly Ni as these mafic phases (particularly olivine) break down during metamorphism. Bevens (1979) and Floyd (1983) use compatible element binary plots ( $Al_2O_3$  vs  $MgO$  and Ni vs Cr respectively) to investigate the nature and identity of the fractionating phases using published solid/melt distribution coefficients and the Rayleigh fractionation Law. However, when the data from the Conwy Valley meta-dolerites are plotted on  $Al_2O_3$  vs  $MgO$  and Ni vs Cr diagrams (Figures 2.13 and 2.14 respectively) a broad scatter is evident probably reflecting the effects of subsequent metamorphism. Also, the recognition of the chemical characteristics of a parent magma is difficult in the Conwy Valley meta-dolerites as the normal assumption that the chilled margin reflects the composition of the parent magma is doubtful as the effects of metamorphism are often very pronounced in the contact zones of many of the intrusions.

Pearce and Norry (1979) use binary plots of the immobile, incompatible elements Zr, Nb, Y and  $TiO_2$  to quantify the effects of crystal fractionation. Using a variety of igneous suites displaying broad ranging fractionation characteristics they quantify the effects of plagioclase, olivine, clinopyroxene, magnetite, orthopyroxene, amphibole and biotite fractionation on incompatible element distribution. In Figure 2.15 the incompatible element data for Meol Siabod is plotted on log graphs on which the calculated mineral fractionation vectors of Pearce and Norry (1979) are also shown. The incompatible element data

FIGURE 2.13. MgO vs  $\text{Al}_2\text{O}_3$  for the meta-dolerite intrusions from the Conwy Valley. Fractionation vectors from Bevins (1979).

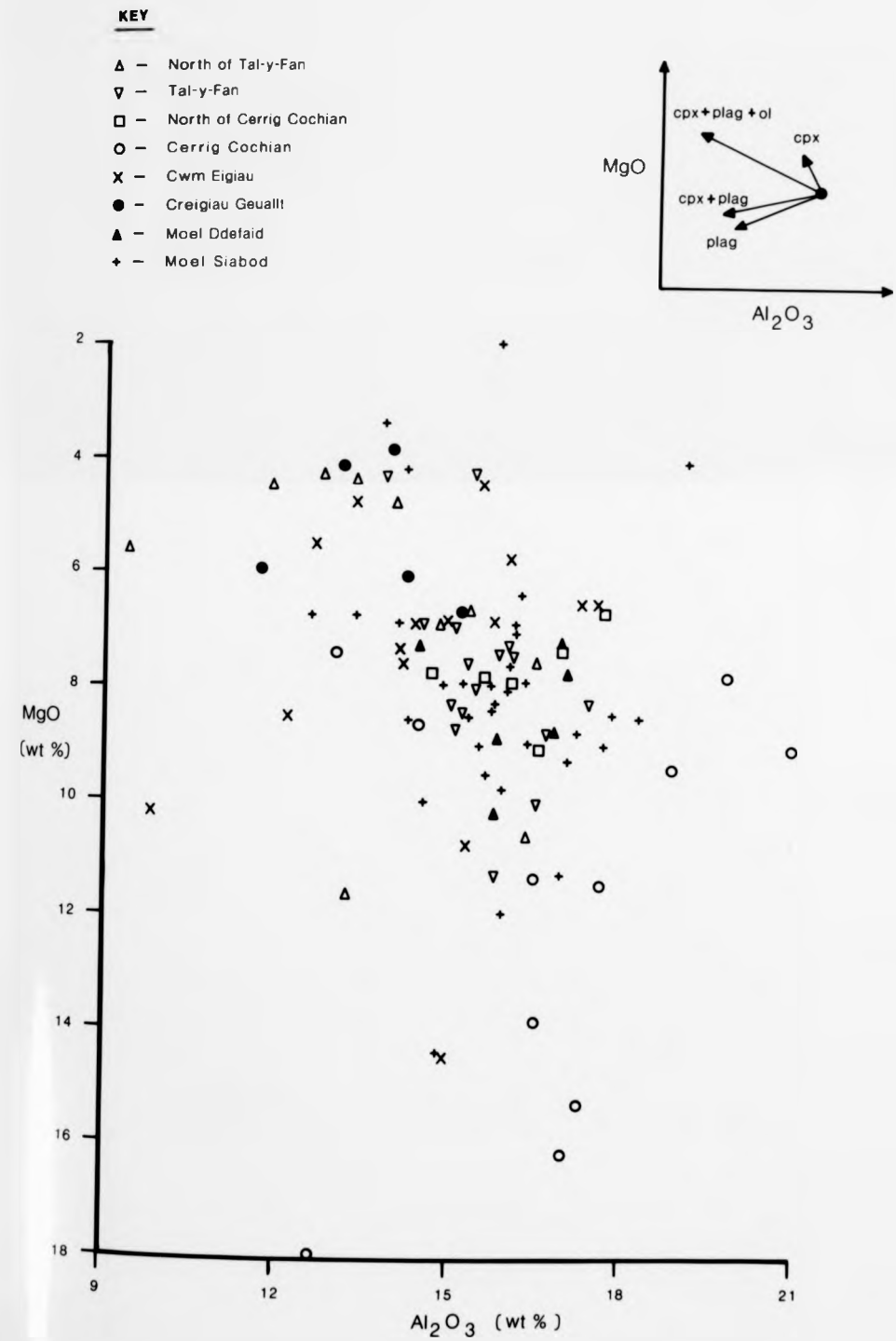


FIGURE 2.14. Ni vs Cr for the Moel Siabod meta-dolerite.  
Fractionation vectors from Floyd (1983).

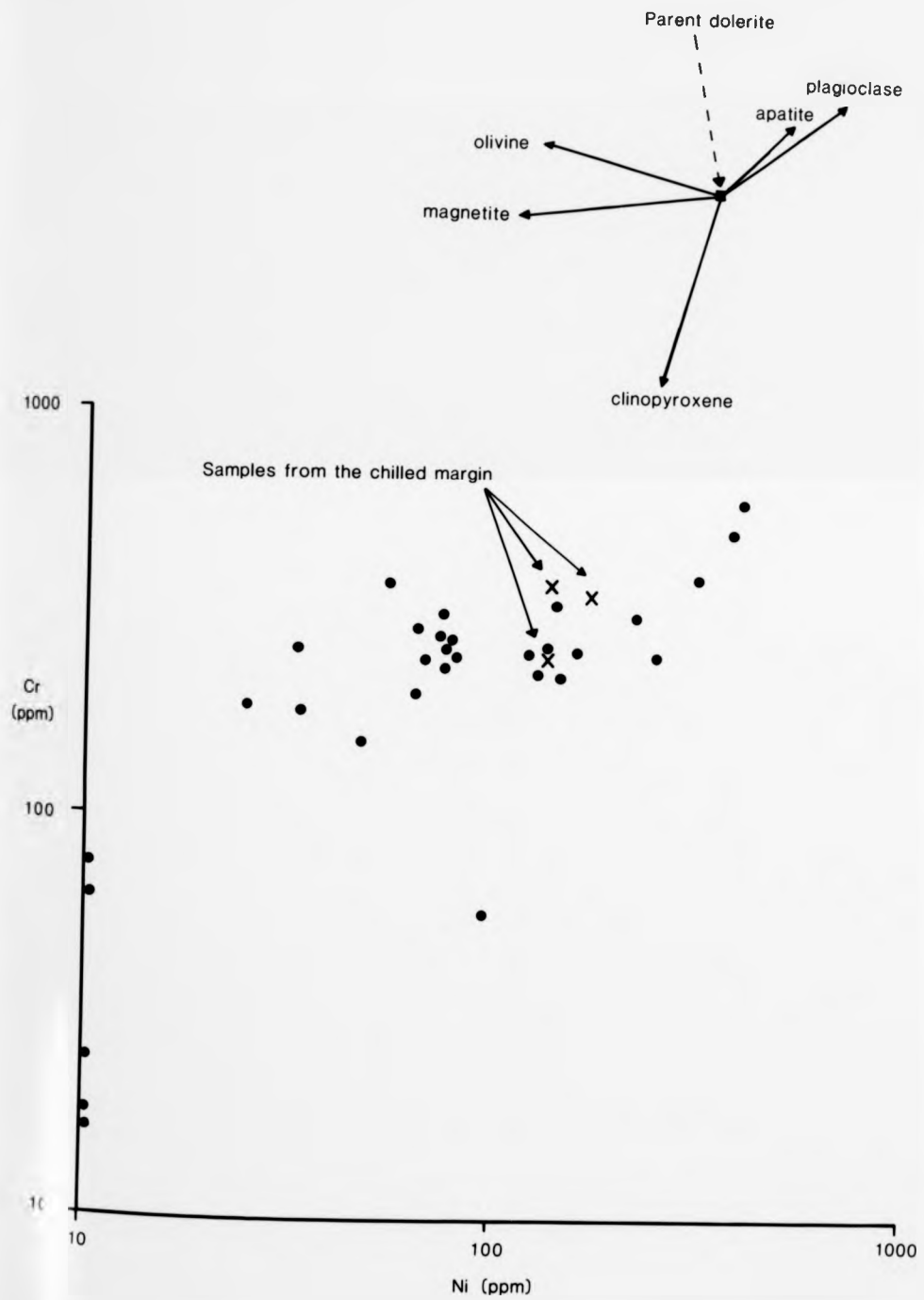
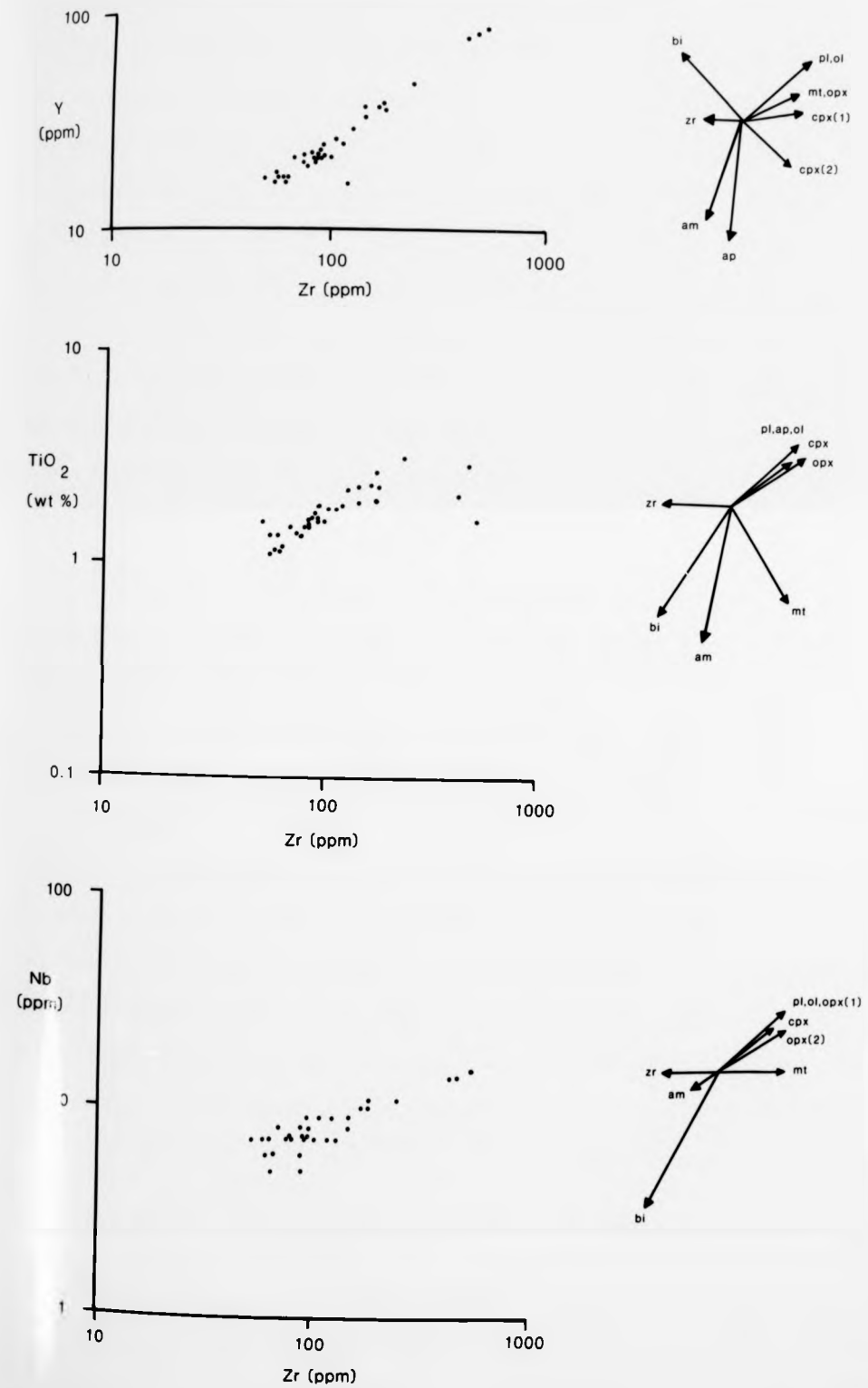


FIGURE 2.15. Log plots of Y vs Zr,  $TiO_2$  vs Zr and Nb vs Zr for the Moel Siabod meta-dolerite. Fractionation vectors are from Pearce and Norry (1979).





indicates that mafic mineral and plagioclase fractionation is responsible for the observed distribution. The major fractionating phases appear to be olivine, clinopyroxene and plagioclase. In the Zr vs  $TiO_2$  plot, in particular, the most differentiated samples (169R1, 169R2 and 179C) display a lower  $TiO_2$  content than might be expected if only olivine, clinopyroxene and plagioclase were fractionating. This trend towards relatively lower  $TiO_2$  in the more differentiated samples reflects the late fractionation of a Ti-bearing phase presumably magnetite. The effects of magnetite fractionation on the Zr vs Nb and Zr vs Y plots would be minimal as magnetite fractionation cannot be readily distinguished on these plots from the effects of plagioclase, clinopyroxene and olivine fractionation.

From the preceding discussion it would appear that primary (magmatic) and secondary (metamorphic) processes have markedly influenced the geochemical characteristics of the meta-dolerites of the Conwy Valley. Once the effects of metamorphism on element mobility and distribution have been assessed it is possible to use those elements least affected by metamorphism to examine the original nature and characteristics of the dolerites. In the Conwy Valley relatively minor chemical differences exist between different intrusions leading to the conclusion that they were derived from a single parent magma or from a series of parent magmas displaying similar geochemical characteristics. Much of the observed variation in immobile elements can be accounted for by olivine, clinopyroxene and plagioclase fractionation with significant magnetite fractionation occurring only in the most differentiated samples.

#### 2.6. Geochemical variation within individual intrusions

In Section 2.5.3. it was shown that much of the primary geochemical variation in the meta-dolerites of the Conwy Valley, reflects the effects of crystal fractionation in variably differentiated dolerite sills.

Figure 2.16. shows the mean  $\text{FeO}^*/\text{MgO}$  ratio for each intrusion, also shown is the  $\text{FeO}^*/\text{MgO}$  one standard deviation which reflects the degree of internal differentiation within the intrusions. From Figure 2.16. it is clear that the more primitive intrusions, displaying relatively low mean  $\text{FeO}^*/\text{MgO}$  ratios, also exhibit little internal differentiation, conversely, the more evolved intrusions, displaying higher mean  $\text{FeO}^*/\text{MgO}$  ratios, exhibit significantly more internal variation. It would appear, therefore, that significant variation in primary geochemical characteristics exist between the intrusions of the Conwy Valley that reflect differences in the degree of differentiation with the development of relatively primitive (Cerrig Cochion) and relatively evolved (Creigiau Geuallt, Cwm Eigiau south) dolerite intrusions. This primary variation in differentiation probably accounts for much of the variation in the less mobile major elements ( $\text{MgO}$ ,  $\text{FeO}^*$ ,  $\text{TiO}_2$  etc.) both between the intrusions and within intrusions displaying evidence for marked internal variation.

Many of the primary and secondary features discussed in Sections 2.4. and 2.5. can be seen in the traverses through some of the larger intrusions. Figure 2.17.1-5 are composite geochemical cross-sections constructed from the chemical data obtained from traverses through the Moel Siabod east, Moel Siabod south, Craig Wen and Tal-y-Fan intrusions, and the small, but petrographically and chemically highly variable, intrusion north of Tal-y-Fan (SH 728725).

From Figures 2.17. 1-5 it would appear that the  $\text{FeO}^*/\text{MgO}$  ratio systematically increases upwards in several of the intrusions. In addition, three of the intrusions contain samples displaying very high ( $> 3.0$ )  $\text{FeO}^*/\text{MgO}$  ratios (the centre of the Tal-y-Fan, the upper margin of Moel Siabod east and the uppermost samples from the small intrusion north of Tal-y-Fan). This latter intrusion (Figure 2.17. 5) most clearly

FIGURE 2.16. Mean FeO\*/MgO ratios  $\pm$  one standard deviation reflecting inter- and intra-intrusion geochemical variation in the meta-dolerites of the Conwy Valley.

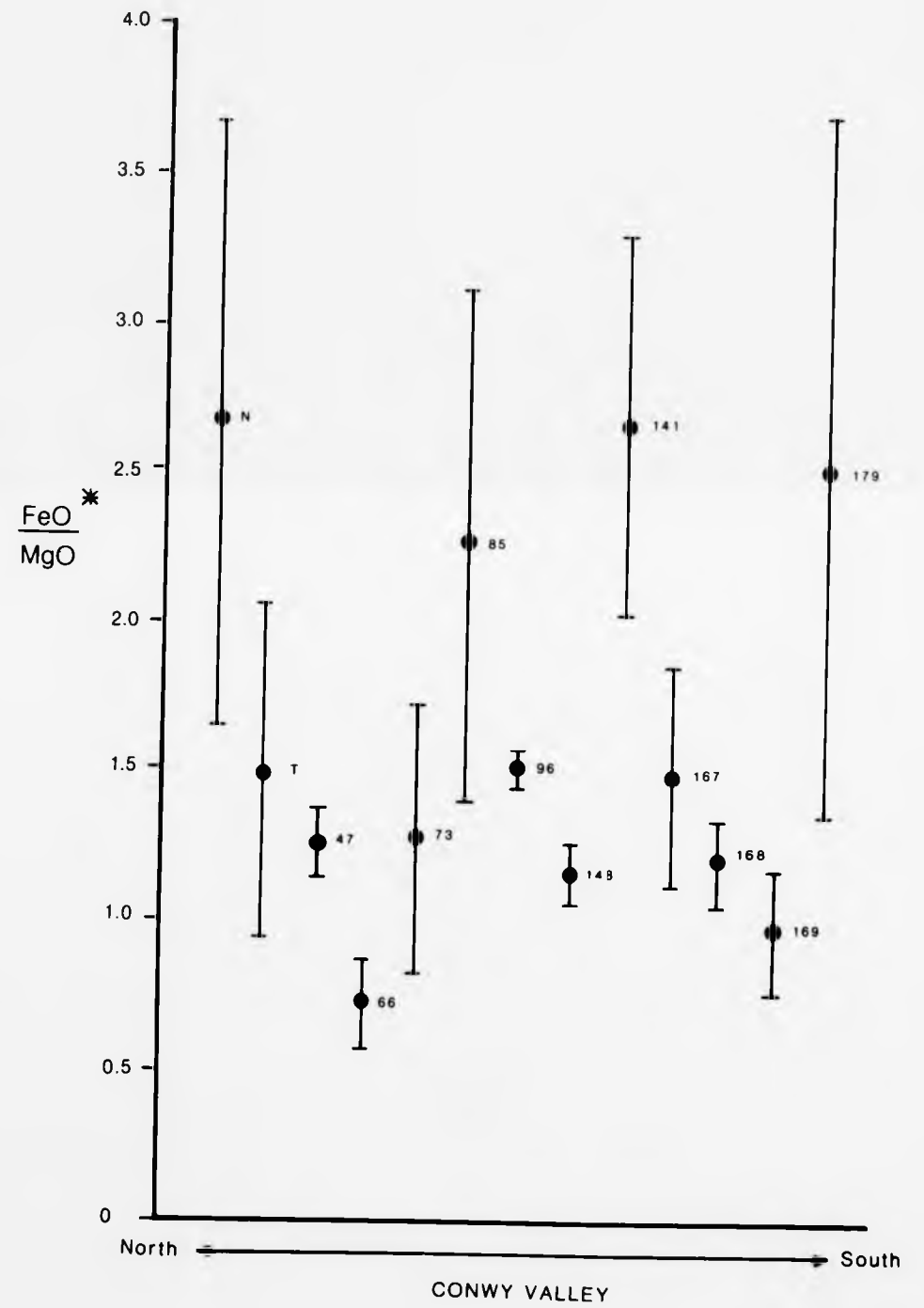


FIGURE 2.17.1. Geochemical traverse through the Moel Siabod (south) intrusion.

FIGURE 2.17.2. Geochemical traverse through the Moel Siabod (east) intrusion.

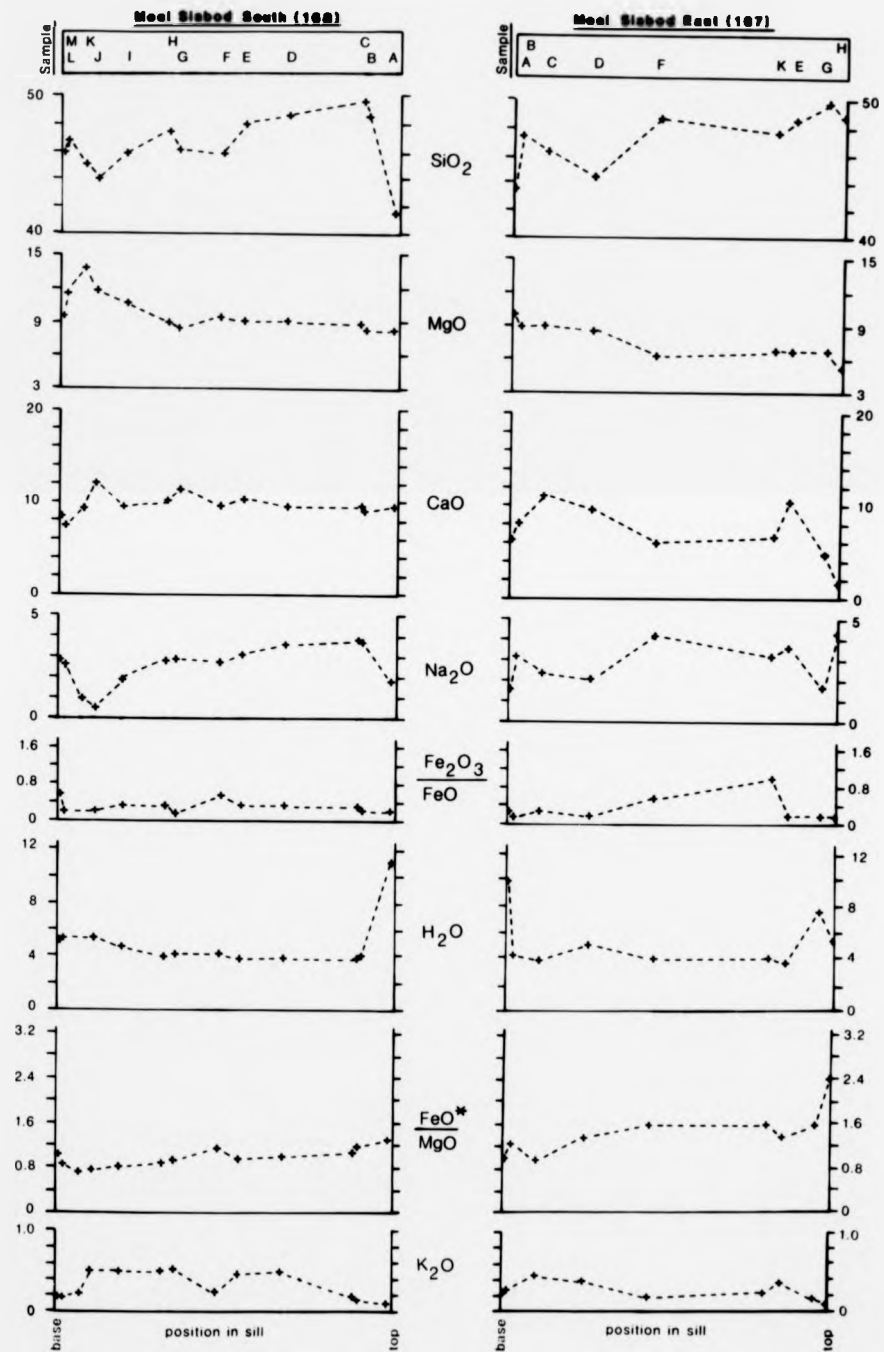


FIGURE 2.17.3. Geochemical traverse through the Tal-y-Fan intrusion.

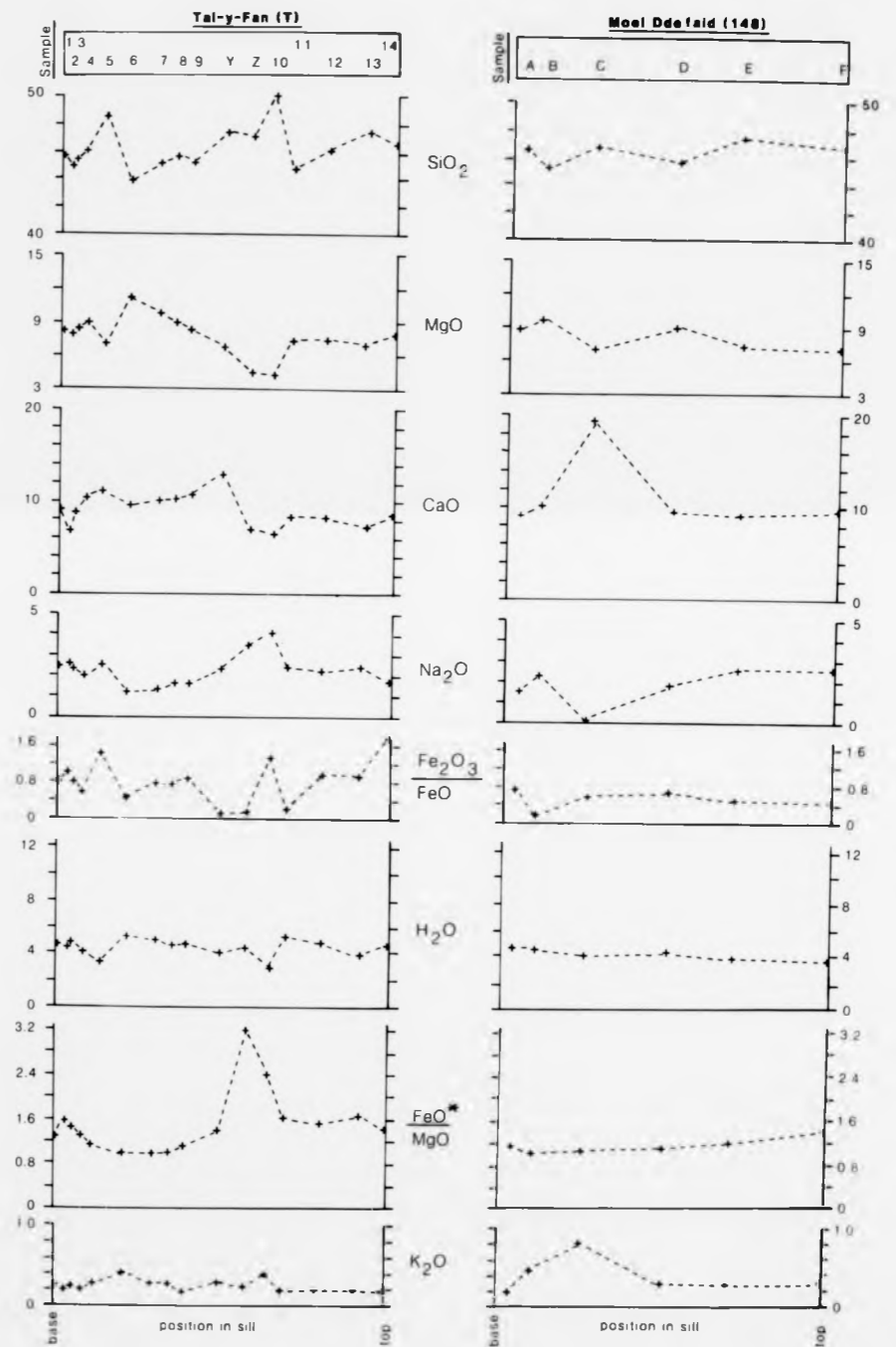
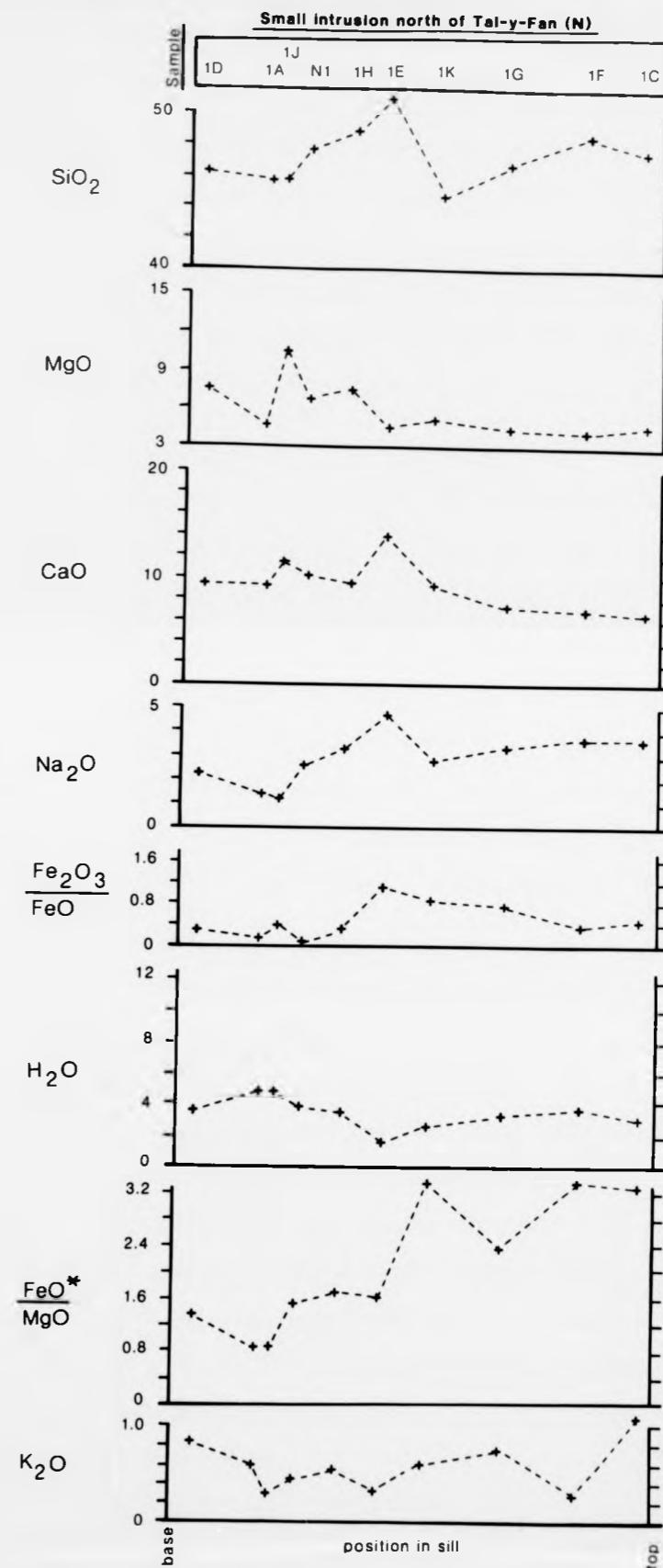


FIGURE 2.17.4. Geochemical traverse through the Moel Ddefaid intrusion.

FIGURE 2.17.5. Geochemical traverse through the small intrusion north of Tal-y-Fan (SH 725728).



displays the effects of variable internal differentiation with samples from the west (base), centre and east (top) displaying progressively higher FeO\*/MgO ratios. Associated with this internal variation in differentiation is a wide range in the relatively less mobile major elements such as TiO<sub>2</sub> (1.12 - 5.61%), FeO\* (7.46 - 19.12%), MgO (4.34 - 11.64%) and P<sub>2</sub>O<sub>5</sub> (0.21 - 1.04%), that still retain many of their primary magmatic geochemical characteristics.

Another interesting feature evident from Figures 2.17. 1-5 is that of relative element depletion and enhancement in the margins of several intrusions. The H<sub>2</sub>O content, for example, is often very high, particularly near the margins of the Moel Siabod intrusions. In addition the SiO<sub>2</sub> content appears to be systematically lower in samples taken from intrusion margins compared to samples taken from within the central part of intrusions. The negative correlations between SiO<sub>2</sub> - H<sub>2</sub>O and Na<sub>2</sub>O - H<sub>2</sub>O and the positive correlations between SiO<sub>2</sub> - Na<sub>2</sub>O and H<sub>2</sub>O - MgO can also be clearly distinguished in the geochemical traverses. These features, particularly the high marginal H<sub>2</sub>O and relatively low marginal SiO<sub>2</sub> content might indicate that these elements have been respectively gained and lost from the intrusions through widespread regional element mobility during low-grade metamorphism. SiO<sub>2</sub>, K<sub>2</sub>O, H<sub>2</sub>O and particularly CaO and Na<sub>2</sub>O vary greatly between samples taken from the same intrusion, possibly indicating that these elements were internally mobilised during low-grade metamorphism. Occasionally CaO in particular is markedly concentrated with several extremely rich samples containing well over 15% CaO. These samples represent sites where CaO, mobilised during low-grade metamorphism, is locally concentrated in Ca rich secondary minerals, particularly epidote. The relationship between geochemistry and petrography in the meta-dolerites of the Conwy Valley is examined more thoroughly in the next Chapter.

### 2.7. Concluding remarks

The 103 major element and 34 trace element analyses undertaken on the meta-dolerites of the Conwy Valley display a large range in chemistry between samples from individual sills, but only a relatively small difference in bulk chemistry between intrusions. Inter-intrusion geochemical variation appears to reflect differences in the amount of primary differentiation and variable element mobility during metamorphism.

It would appear from the good correlation between  $H_2O$  and  $SiO_2$ ,  $MgO$ ,  $Na_2O$ ,  $Rb$ ,  $Sr$  and  $Ba$  that these elements may have been regionally mobilised during hydration. In addition oxides such as  $K_2O$ ,  $SiO_2$ ,  $Na_2O$  and, particularly,  $CaO$ , appear to have been markedly mobile within the intrusive bodies with relative depletion in parts of the intrusion and corresponding, often quite extreme, enrichment in others. Good correlation between the immobile trace elements ( $Y$ ,  $Zr$  and  $Nb$ ) and  $TiO_2$ ,  $FeO^*$ ,  $MnO$ ,  $P_2O_5$ ,  $La$ ,  $Ce$  and  $Nd$  indicated that these elements have behaved in an essentially immobile, or only slightly mobile way on anything other than the very small scale during low-grade metamorphism. The good correlation between  $TiO_2$ ,  $Y$ ,  $Zr$  and  $Nb$  and the  $FeO^*/MgO$  ratio indicates that this too has remained relatively stable and can, therefore, be reliably employed as an index of differentiation.

The immobile major and trace element geochemical characteristics indicate that the meta-dolerites are derived from a differentiated tholeiitic magma. There are no systematic differences in incompatible element geochemistry between intrusions indicating that they are derived from one tholeiitic parent magma or that if more than one parent magma was involved they were compositionally very similar. Much of the primary geochemical variation can be accounted for by crystal fractionation with the major fractionating phases being olivine, clinopyroxene



and plagioclase and, in the latest stages, magnetite.

In the following two chapters the geochemical results are utilised in the interpretation of the petrographic observations, where the relationships between geochemistry and petrography are examined, and as a data base to evaluate the role of host rock compositional control on metamorphic phase chemistry.

## CHAPTER 3

### PETROGRAPHY OF THE META-DOLERITES

#### 3.1. Introduction

An essential feature in any metamorphic area is detailed and systematic petrographic observation. Microscopic observation of low-grade metamorphic rocks often provides valuable information concerning the primary mineralogy and the nature, distribution and variation of secondary minerals and the possible nature and direction of metamorphic reactions.

In the present study detailed petrographic observations were undertaken on the widely distributed meta-dolerites of northern Snowdonia. Other lithologies were examined in much less detail. In all, 194 meta-dolerites were examined, 103 of these corresponding to samples on which bulk rock chemical analyses were obtained. The other 91 samples are representative of the remaining intrusions of the Conwy Valley and central northern Snowdonia. The locations of samples used in the petrographic study are listed in Appendix 2(i). The petrographic observations examine the effects of low-grade metamorphism in rocks of broadly similar composition where alteration and recrystallisation has been incomplete. Geochemical control is provided by the bulk rock data of the last Chapter and contained in Appendix 3(i).

It was hoped that the petrographic observations would provide information concerning characteristic secondary mineral assemblages developed within the meta-dolerites, and distinguish any variation in metamorphic assemblage on the small scale (within the area of a thin section), the medium scale (within an intrusion) and the relatively large scale (within northern Snowdonia). These observations could

then be used to allow some quantification of the parameters of metamorphism (pressure, temperature, fluid composition etc.,) and to attempt a correlation with other low-grade metamorphic indicators. Observation concerning the nature and intensity of alteration indicates the relative control of the fluid on metamorphic recrystallisation. Together with the geochemical results it should be possible to evaluate the influence of bulk rock chemistry on the development and nature of the secondary minerals. In addition the petrographic and mineral chemical data have been used to assess, semi-quantitatively, textural and chemical equilibrium and provide some indication of the scale over which equilibrium can be said to have been attained.

### 3.2. Relict mineralogy

Although the basic intrusions of northern Snowdonia have suffered, to a greater or lesser extent, some low-grade metamorphism, their original mineralogy has been only partially obliterated. The present mineralogy consists largely of augitic pyroxene, albitised plagioclase, chlorite and small amounts of sphene, with variable amounts of two or three of the following phases, quartz, calcite, prehnite, epidote, actinolite, white mica, pumpellyite and stilpnomelane. Clearly these mineralogical characteristics are largely of a secondary nature and compare, at least superficially, with the typical "spilitic" mineral assemblages described by Vallance (1965); Miyashiro et al. (1971) Humphris and Thompson (1978), and so on, that are typical of low-grade metamorphism of basic rocks.

The augitic pyroxene is considered to be a metastable, relict, igneous phase that has typically survived low-grade metamorphism with only relatively minor alteration, generally to actinolitic amphibole and occasionally to chlorite. Clinopyroxenes have been shown to persist during low-grade metamorphism, for example, in South Wales by Bevins

(1979) and throughout Wales by Bevins and Rowbotham (1983). Recently, Schiffman et al. (in press) have described metamorphic clinopyroxene forming in stable association with typical greenschist facies assemblages for example, i) epidote + actinolite + clinopyroxene, and ii) epidote + biotite + actinolite + clinopyroxene. However, these new clinopyroxenes occur in calc-silicate rocks in an active geothermal field ( $P = < 1\text{ kb}$ ,  $T = 250^{\circ}\text{C}$ ) and are, therefore, quite distinct from the relict igneous clinopyroxenes preserved in northern Snowdonia. It may be, however, that the P/T stability field of clinopyroxene is approached during low-grade metamorphism (particularly at high relative temperatures) thus possibly accounting for the frequent persistence of clinopyroxene in the low-grade metamorphic environment.

Albitised feldspar is ubiquitous and typically replaces igneous plagioclase precipitated in equilibrium with clinopyroxenes with which it is frequently optically intergrown (Figure 3.1.1). Occasionally plagioclase crystals display extinction angles of up to  $32^{\circ}$  (010 to  $\alpha$ ) indicating a labradoritic composition. However, extinction angles of over  $20^{\circ}$  are rare and crystals displaying such high extinction angles are generally small. In several samples plagioclase displays marked compositional zoning, again indicating a relict calcic igneous plagioclase. Finally, microprobe analysis confirms the presence of labradoritic plagioclase in samples 66A and 66I with a maximum anorthite content of 60% ( $\text{An}_{60}$ ). It would appear, therefore, that the original igneous plagioclase was labradoritic in composition which has been subsequently albitised during low-grade metamorphism. Relict calcic plagioclase feldspars have been described from Welsh meta-dolerites by Howells et al. (1978) and Bevins and Rowbotham (1983).

Much of the sphene present within the meta-dolerites is thought to reflect the alteration of an original Ti-Fe ore phase. Often sphene

FIGURE 3.1.1. Relict ophitic intergrowth of plagioclase (white) (Upper left) with pyroxene (black), sample 47D (central Conwy Valley). XP. X10.

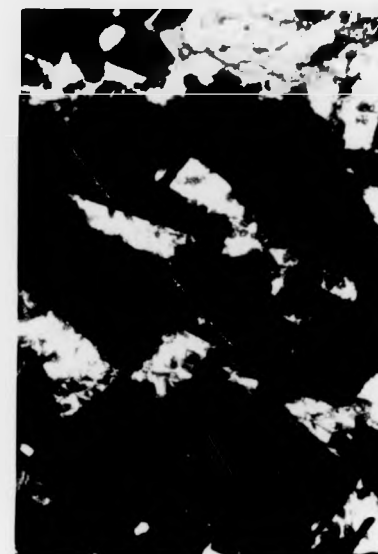


FIGURE 3.1.2. Exsolution and alteration in the ores with magnetite (black) intergrown with ilmenite, now altered to sphene (very dark grey), sample TZ (Tal-y-Fan). PPL. X63.

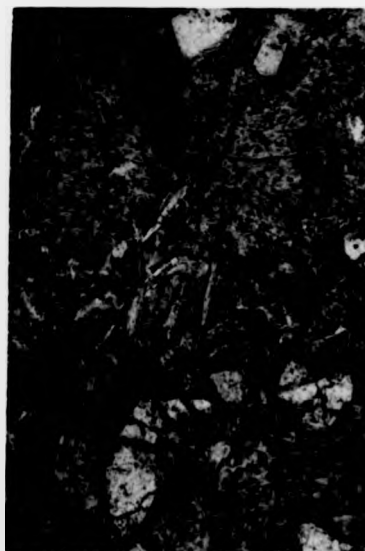


FIGURE 3.1.3. Interstitial alteration site containing chlorite (medium grey), epidote (light grey) and acicular actinolite (needles), sample 168G (Moe1 Siabod). PPL. X63.

FIGURE 3.1.4. Sub-rounded chlorite pseudomorphing an original (Lower right) olivine, sample 66D (Cerrig Cochion). PPL. X10.

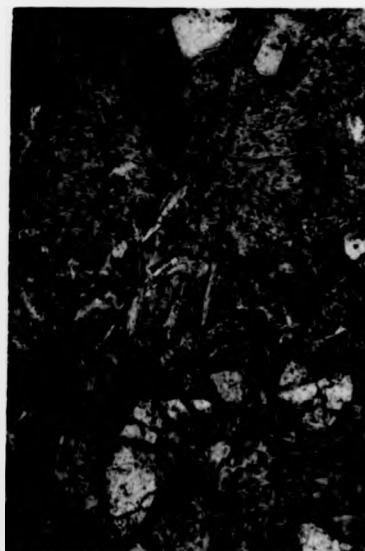


FIGURE 3.1.1. Relict ophitic intergrowth of plagioclase (white) (Upper left) with pyroxene (black), sample 47D (central Conwy Valley). XP. X10.

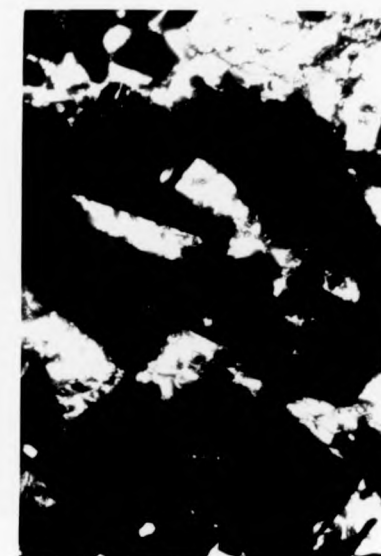


FIGURE 3.1.2. Exsolution and alteration in the ores with magnetite (black) intergrown with ilmenite, now altered to sphene (very dark grey), sample TZ (Tal-y-Fan). PPL. X63.

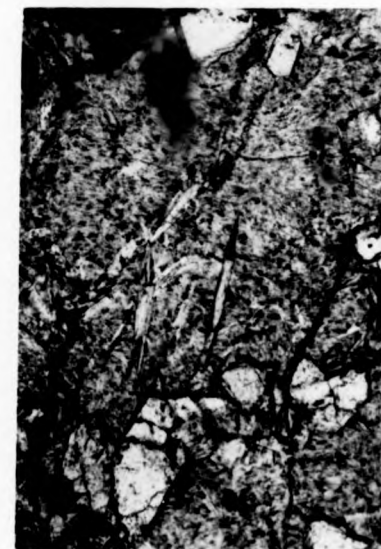


FIGURE 3.1.3. Interstitial alteration site containing chlorite (medium grey), epidote (light grey) and acicular actinolite (needles), sample 168G (Moe1 Siabod). PPL. X63.

FIGURE 3.1.4. Sub-rounded chlorite pseudomorphing an original olivine, sample 66D (Cerrig Cochion). PPL. X10.

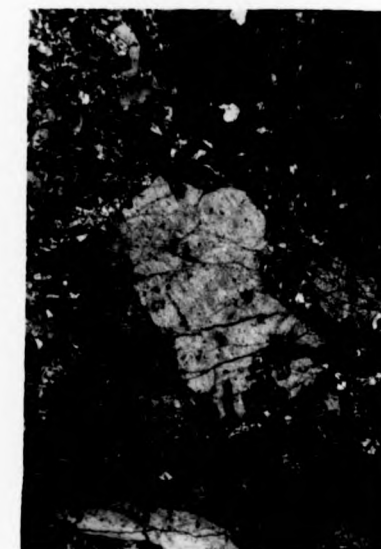
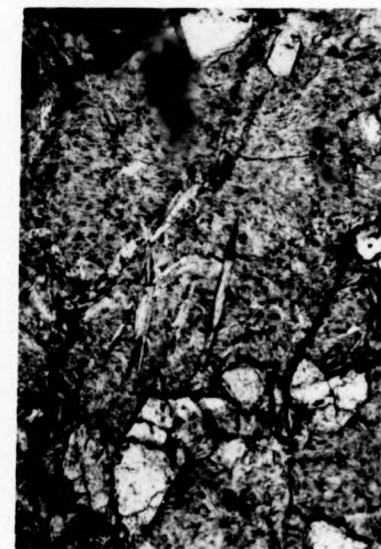
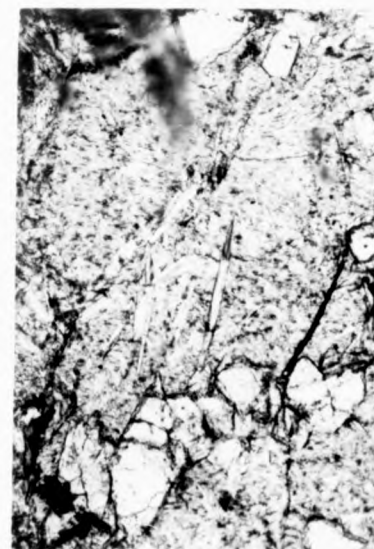


FIGURE 3.1.1. Relict ophitic intergrowth of plagioclase (white) (Upper left) with pyroxene (black), sample 47D (central Conwy Valley), XP, X10.

FIGURE 3.1.2. Evolution and alteration in the ores with magnetite (black) intergrown with ilmenite, now altered to sphene (very dark grey), sample TZ (Tal-y-Fan), PPL, X63.

FIGURE 3.1.3. Interstitial alteration site containing chlorite (medium grey), epidote (light grey) and acicular actinolite (needles), sample 168G (Moel Siabod), PPL, X63.

FIGURE 3.1.4. Sub-rounded chlorite pseudomorphing an original olivine, sample 66D (Cerrig Cochion), PPL, X10.



pseudomorphs the original ore phase and occasionally there is evidence that the ores had exsolved into Ti-rich (ilmenite) and Fe-rich (magnetite) phases, the former now being pseudomorphed by sphene whilst the latter remains relatively unaltered (Figure 3.1.2.).

In addition to the phases outlined above, the meta-dolerites contain significant amounts of interstitial chlorite often associated with one or more other secondary phases (Figure 3.1.3). The origin of this interstitial material is not clear, however, the textural evidence is consistent with the view that these chlorite interstitial areas represent the products of mesostasis with late magmatic material trapped in the interstitial areas between the earlier formed coarser grained crystals. Small sphene and brown amphibole crystals are frequently present within these areas and occasionally small clinopyroxene crystals can also be distinguished.

Finally, in a number of samples, particularly the least differentiated samples from Tal-y-Fan and Cerrig Cochion, pseudomorphs of chlorite replacing olivine occur (Figure 3.1.4). In the meta-dolerites of northern Snowdonia no fresh or relict olivine was found. Further west, in the layered mafic intrusions of the Llyn peninsula (Rhiw, Mynydd, Penarfynydd, etc.,) which have undergone slightly lower grade metamorphism (Roberts, 1981), relict igneous olivine is abundant.

The meta-dolerites of northern Snowdonia display a range of igneous textures often discernible despite the low-grade metamorphism. By far the most frequently developed texture is that of ophitic or sub-ophitic intergrowth of plagioclase and clinopyroxene (Figure 3.1.1). Occasionally cumulate or sub-cumulate textures are preserved where the cumulate phase is generally pyroxene or, more rarely, olivine (now replaced). Grain size in the meta-dolerites is extremely variable and ranges from very fine grained doleritic through to coarsely gabbroic (Cerrig Cochion)



and occasionally pegmatitic (parts of Moel Siabod). Grain size appears to be largely independent of intrusion size or position within the intrusion. In the contact zones of many intrusions a narrow (usually less than a metre), fine grained, chilled margin is developed.

Compositional variation between samples is reflected by differences in the relative proportions of relict clinopyroxene, albitised plagioclase and interstitial material, and through the presence of chlorite pseudomorphs after olivine. The presence of occasional normal zoning in relict calcic plagioclase and clinopyroxene, for example in samples from the St. Celynin intrusion 2 km east of Tal-y-Fan (Samples 38A-H) reflect the progressive change in magma composition throughout the crystallisation of these phases.

### 3.3. Secondary mineralogy

#### 3.3.1. Bulk alteration characteristics

In the current study the following secondary mineral phases were recognised, prehnite, pumpellyite, actinolite, epidote, white mica, albite, stilpnomelane, chlorite, quartz, calcite, sphene and (?) biotite, of these albite, chlorite and epidote are volumetrically the most significant. Within the samples of meta-dolerite from northern Snowdonia four characteristic types of alteration have been distinguished, reflecting the relative abundance of chlorite, albite and epidote. The four categories of meta-dolerite are the characteristic hydrated meta-dolerite and the more extreme chlorite, albite and epidote rich meta-dolerites, accounting for 49%; 24%; 16% and 11% of the samples respectively. Broad classification of the samples in this way is clearly subjective. Continuous gradation exists between samples belonging to the different meta-dolerite categories.

The general petrographic characteristics displayed by samples of

the different types of meta-dolerite are:-

i) Hydrated - moderate amounts of chlorite, albite and, often, epidote with varying, but typically small, amounts of hydrous Ca/Al silicates, actinolite, white mica, calcite and quartz. Relict clinopyroxene is abundant and variably altered with only occasional internal alteration to chlorite or actinolite, many samples display minor epitaxial actinolite overgrowth. Plagioclase is variably albitised and contains a variety of secondary phases including prehnite, pumpellyite, epidote and white mica. Ore minerals are variably altered. Hydrated dolerite samples occasionally display weak oriented fabrics.

ii) Albite rich - abundant albitised plagioclase reflecting a high primary plagioclase content. Moderate amounts of chlorite, calcite, quartz and stilpnomelane and typically small quantities of epidote also occur. Other secondary phases are relatively scarce. Clinopyroxene is often relatively fresh with little alteration to either chlorite or amphibole. Plagioclase is typically thoroughly albitised containing minor white mica or epidote, the ores are relatively unaltered. These samples generally appear little altered and never display oriented fabrics.

iii) Chlorite rich - abundant chlorite with moderate amounts of the hydrous Ca/Al silicates, actinolite, epidote and white mica and typically small amounts of calcite and quartz. The original plagioclase is often thoroughly replaced, often by chlorite, and contains variable amounts of the hydrous Ca/Al silicates. Clinopyroxene often displays significant epitaxial actinolite overgrowth and the development of internal chlorite veins. Ore minerals are also typically heavily altered. Recrystallisation in these samples is marked and many of the samples have developed an oriented metamorphic fabric.

iv) Epidote rich - abundant epidote with moderate or small amounts of albite, chlorite and stilpnomelane. Other secondary minerals are relatively scarce. Clinopyroxenes and the ores are often relatively unaltered. Plagioclase is thoroughly albitised and often contains small crystals of epidote. These samples do not develop oriented fabrics with the abundant epidote occurring as randomly oriented prismatic crystals.

The differences in alteration characteristics are thought to reflect the effects of both primary magmatic variation and subsequent differences in alteration between samples. Albite and chlorite rich samples represent the most and least fractionated samples respectively (relative to the hydrated meta-dolerite samples).

No systematic relationship exists between the epidote rich samples and fractionation and these samples probably reflect the local concentration of Ca mobilised during metamorphism. The relationship between geochemistry and bulk alteration characteristics is discussed in more detail in Section 3.7.2.

Diagnostic low-grade prehnite  $\pm$  pumpellyite  $\pm$  actinolite  $\pm$  epidote bearing assemblages are best developed in samples of the hydrated and chlorite rich meta-dolerites, the albite and epidote rich meta-dolerites tend to contain assemblages lacking the diagnostic, low-grade, secondary phases.

### 3.3.2. Secondary mineral assemblages

The results of the petrographic observations are shown in Appendix 4 where the secondary mineral assemblages identified for each sample are listed. These are based on observations on a standard thin section. Some attempt is made to distinguish between the volumetrically major and minor phases, those showing evidence of breakdown and zoned phases

(particularly epidotes).

Chlorite, sphene and plagioclase feldspar are ubiquitous (Appendix 4) although the feldspar is occasionally a relict igneous phase. Epidote is frequently developed although its optical properties are highly variable, ranging from yellow and pleochroic ( $\alpha$  = colourless,  $\beta$  = yellow,  $\gamma$  = yellow ) pistacitic epidote to colourless and non-pleochroic clinozoisitic epidote. In addition, many of the epidotes are optically continuously zoned from a more pistacitic core to a less pistacitic rim, an observation confirmed by microprobe analyses in the next chapter. Of the remaining secondary phases calcite, quartz and white mica are widespread throughout northern Snowdonia whilst stilpnomelane is only sporadically developed in the more fractionated rocks (Section 3.7.3). Biotite was only recognised in one sample and whether it was relict or secondary is uncertain. Prehnite, pumpellyite and actinolite, therefore, appear to be the critical secondary mineral phases whose development might be related to metamorphic conditions, an interpretation consistent with observations from other areas of low-grade metamorphism by, for example, Hawkins (1967); Coombs et al. (1970); Bishop (1972); Zen (1974) and Bevins and Rowbotham (1983). The development of Fe-poor epidote (clinozoisite) has also been related to metamorphic conditions by Liou (1973) and Liou et al. (1983). However, due to the optical variability of the epidotes, outlined above, and the necessity for precise compositional data a thorough discussion of the epidotes is delayed until Chapter 4. Petrographically epidotes were divided into: i) pistacite, where they are yellow and pleochroic and display second or third order birefringence colours, ii) clinozoisite, where they are colourless and display first order grey or anomalous blue birefringence colours, and iii) zoned epidotes.

A simplified mineral assemblage map constructed from the observ-

ations relating to the presence of prehnite; pumpellyite and actinolite (Figure 3.2) and a map summarising the petrographic observations for the epidotes (Figure 3.3) are included as separate sheets.

### 3.4. Variation in secondary mineral assemblage

The variation in secondary mineral assemblages and the nature of alteration can be examined on: i) the regional scale (that observed throughout northern Snowdonia), ii) the local scale (that observed within an individual intrusion) and, iii) the small scale (that observed within a single thin section).

#### 3.4.1. Regional variation

Six potentially diagnostic secondary mineral assemblages are identified (Figure 3.2) based on the development and association of prehnite, pumpellyite and actinolite. The mineral assemblages are:-

- i) prehnite + pumpellyite (without actinolite)
- ii) prehnite + pumpellyite + actinolite
- iii) prehnite + actinolite (without pumpellyite)
- iv) pumpellyite (without prehnite or actinolite)
- v) pumpellyite + actinolite (without prehnite)
- vi) actinolite (without prehnite or pumpellyite)

These assemblages approximate to the transition from the prehnite-pumpellyite facies (group i), through the pumpellyite-actinolite facies (group v) and into the greenschist facies (group vi), of low-grade metamorphism (Turner, 1981).

From Figures 3.2. and 3.3. it can be seen that a significant amount of variation exists in secondary mineral assemblages within northern Snowdonia. One particularly clear feature is the distribution of relatively "higher" and "lower" grade assemblages, with the lower

grade assemblages (prehnite bearing) being present predominantly in the northern Conwy Valley. Significant quantities of prehnite occur in the central Conwy Valley, particularly the Cerrig Cochion intrusion. However, much of this prehnite appears to be unstable with the development of clouding and diffuse crystal outlines (Samples 66H and 66I), or present as part of a disequilibrium assemblage (Samples 66C and 66F). Typical secondary mineral assemblages for these prehnite bearing samples include:-

Chlorite + albite + prehnite + pumpellyite + white mica + (actinolite)  
chlorite + albite + epidote + prehnite + pumpellyite + sphene.

In addition to these typically low-grade prehnite-pumpellyite facies assemblages there are samples in which prehnite and actinolite are associated, for example:-

Chlorite + albite + epidote + prehnite + pumpellyite + actinolite + white mica + sphene.

Chlorite + albite + prehnite + actinolite + white mica + sphene.

Prehnites in several of the samples in which prehnite and actinolite coexist display evidence of breakdown or are present as part of a disequilibrium assemblage (see Section 3.6). These assemblages might reflect slightly higher metamorphic grade with the prehnite being either a meta-stable, lower grade phase, or present in the highest grade part of its stability range where the stability fields of prehnite and actinolite overlap (Zen, 1974; Schermerhorn, 1975; Schiffman and Liou, 1980). Experimental and thermodynamic studies by Zen (1974) and Schiffman and Liou (1980) indicate that the stable coexistence of prehnite and actinolite represents the highest grade of sub-greenschist metamorphism and occurs over a restricted P - T range. Most observations of coexisting prehnite and actinolite have been made in areas of

relatively high geothermal gradient.

In the southern and central Conwy Valley prehnite is only very rarely observed (2 samples) with pumpellyite and, particularly, actinolite becoming the dominant diagnostic secondary phases. Between Cerrig Cochion and Moel Siabod actinolite is extensively developed with only the sporadic development of pumpellyite, and even then only in small amounts. Typical secondary mineral assemblages from the central Conwy Valley include:-

Chlorite + albite + epidote + actinolite + sphene + (pumpellyite).

Chlorite + albite + epidote + actinolite + sphene + white mica.

The coexistence of actinolite  $\pm$  minor pumpellyite could reflect metamorphism either in the high-grade part of the pumpellyite-actinolite facies or low-grade part of the greenschist facies (Schiffman and Liou, 1980) or the effects of disequilibrium on the scale of the thin section.

South of Moel Siabod the amount of pumpellyite increases again with over half the samples containing some pumpellyite. Actinolite remains an important constituent.

These general observations are broadly consistent with those of Roberts (1981) who describes prehnite and pumpellyite bearing assemblages in the northern Conwy Valley; dominantly actinolite and clinozoisite bearing assemblages in the central Conwy Valley and pumpellyite, epidote and actinolite bearing assemblages in the southern Conwy Valley.

In central northern Snowdonia the dominant assemblages are almost exclusively actinolitic with only one sample containing any pumpellyite. In this respect these samples are similar to those of the central Conwy Valley.

Clinozoisite is the dominant epidote in the central Conwy Valley

(Figure 3.3) with pistacitic epidote well developed in the northern Conwy Valley, central northern Snowdonia and the southern Conwy Valley. The distribution of pistacitic and clinozoisite epidote does not correlate with the distribution of prehnite, pumpellyite and actinolite, with lower grade pistacitic epidote (Liou et al., 1983) being associated with some of the lowest grade samples (prehnite and pumpellyite bearing) in the far north and some of the highest grade (actinolite bearing) samples of the central Conwy Valley and central northern Snowdonia. In the southern Conwy Valley the pattern is further complicated by the presence of extensive optical zoning within the epidotes. It would appear, therefore, that no simple petrographic relationship exists between the epidotes and the distribution of the critical prehnite, pumpellyite and actinolite assemblages.

#### 3.4.2. Local and small-scale variation

In addition to the broad regional variation in the distribution of secondary mineral assemblages, significant variation exists within individual intrusions. In all the intrusions from which a number of samples were taken there is a range in secondary mineral assemblages and sub-assemblages, particularly in terms of the diagnostic low-grade minerals prehnite, pumpellyite, actinolite and epidote, and the presence of minerals such as calcite, quartz and stilpnomelane. There is also significant variation in the nature of alteration both on the intrusion and hand specimen scale.

Variation in secondary mineralogy within an individual intrusion is particularly pronounced in the intrusions of the northern Conwy Valley, Cerrig Cochion and parts of Moel Siabod. The close spatial association of a variety of normally diagnostic secondary mineral assemblages is problematical. However, an important feature would appear to be the greater relative variation in the areas of lowest grade with less



variation in areas of higher grade (Section 3.5. and 3.8).

The epidotes tend to be relatively consistent on the small-scale (Figure 3.3) with individual intrusions generally containing optically similar epidotes. Moel Siabod is an exception and appears to display a wide range in epidote optics, much of this variability, however, reflects epidote zoning.

Occasionally variation in the nature of alteration can be seen within the area of a thin section. Sample 168E provides a clear example of this with the primary plagioclase having altered to albite + white mica over 25% of the slide and albite + epidote + pumpellyite over the remaining 75% of the slide. Clearly this heterogeneity in the nature of alteration must represent differences in small-scale chemistry. Where plagioclase is altering to albite + white mica elements such as Ca and Al must leave the site of alteration. Where plagioclase is altering to albite + epidote  $\pm$  pumpellyite the excess Ca and Al will be incorporated in the epidote and pumpellyite. However, both these phases require the introduction of Fe from an external source into the plagioclase sites. It is possible, therefore, that the supply of external Fe, which must reflect the breakdown of an Fe-rich phase (ore, clinopyroxene, etc), and its subsequent transport into the plagioclase site, might control the nature of alteration, so that without a supply of Fe into the plagioclase albite + white mica will develop rather than albite + epidote  $\pm$  pumpellyite.

Two other samples (168B and 168C) display heterogeneous alteration characteristics on the hand specimen scale with the development of metamorphic domains (Smith, 1968) that are relatively richer and poorer in chlorite. Other than the proportion of chlorite, the main difference between the domains is the quantity of relict igneous pyroxene with the chlorite rich areas containing relatively little pyroxene. It would thus

seem possible that the breakdown of pyroxene controls the nature of alteration, with the variable breakdown of pyroxene possibly reflecting variation in the passage of fluid through the rock. Occasionally, where pyroxene does occur in the chlorite rich areas of these samples, it appears to be relatively fresh and does not appear to be heavily altered. It is possible, therefore, that there was some original mineralogical heterogeneity within the meta-dolerites which has also influenced the nature of subsequent alteration.

From the above discussion it is clear that variation in alteration on the small-scale is governed by the relative abundance and breakdown of primary constituents. Heterogeneity in alteration may reflect mineralogical variation within the fresh dolerites, and hence the availability of specific primary phases for alteration, or relative differences in the effects of alteration on the primary constituents, which might reflect differences in fluid conditions both within and between samples.

### 3.5. Secondary minerals and sites of alteration

The secondary minerals discussed so far have been identified over the area of a standard thin section. However, it is evident that alteration is heterogeneous and often closely reflects the primary igneous mineralogy, with individual primary mineral sites containing distinct secondary mineral sub-assemblages. Five possible primary alteration sites have been identified, viz: clinopyroxene, plagioclase feldspar, olivine, ore and interstitial.

#### i) Clinopyroxene sites

Clinopyroxene is the only igneous mineral frequently preserved as a relict phase (Section 3.2). Only two types of clinopyroxene alteration have been observed in northern Snowdonia these being alteration to either

FIGURE 3.4.1. Epitaxial overgrowth of amphibole (white) around pyroxene (black), sample 168J (Moel Siabod). XP. X16.

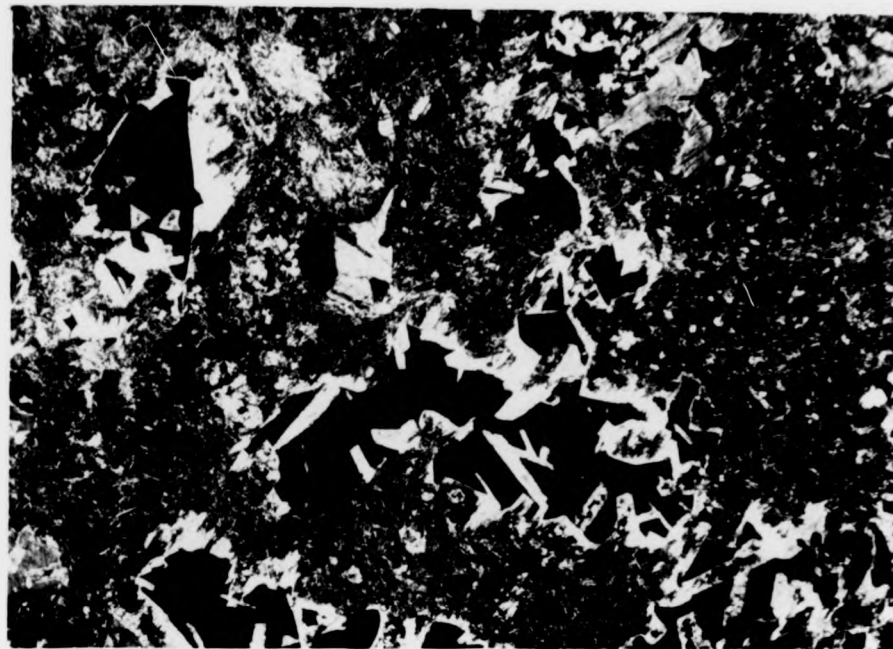


FIGURE 3.4.2. Pyroxene (dark grey) being replaced by chlorite (light grey) along fractures, sample 167K (Moel Siabod). PPL. X100.

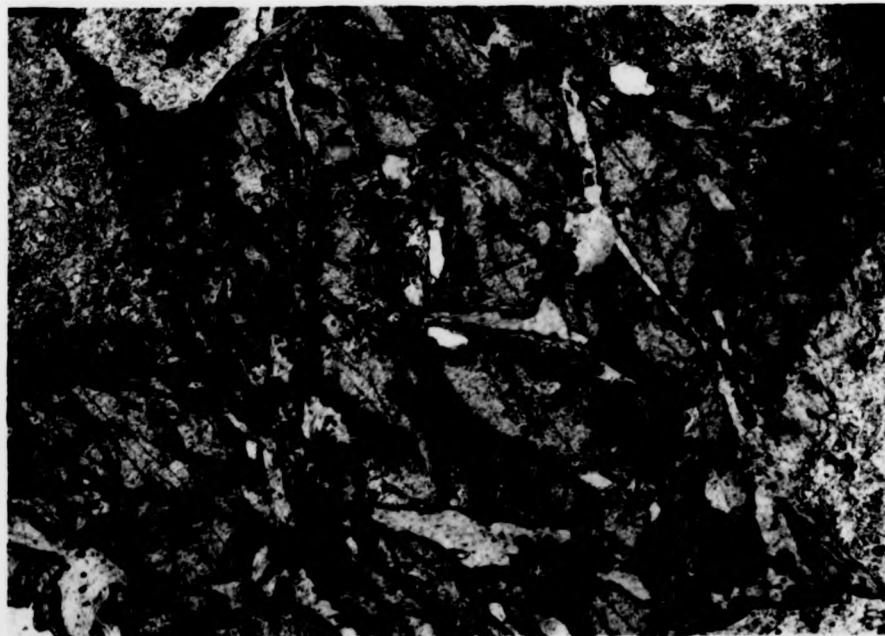


FIGURE 3.4.1. Epitaxial overgrowth of amphibole (white) around pyroxene (black), sample 168J (Moel Siabod). XP. X16.

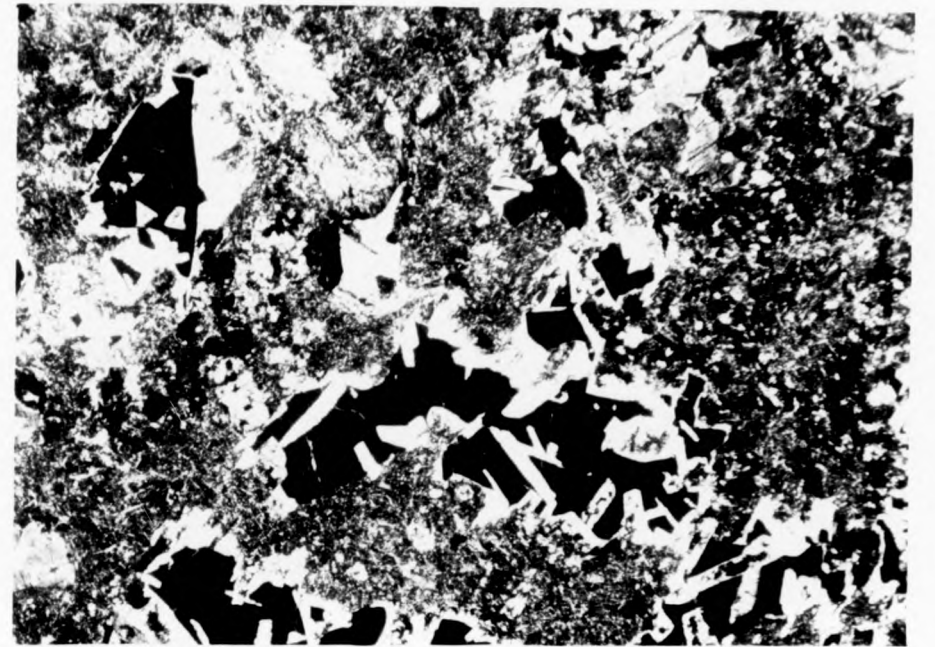
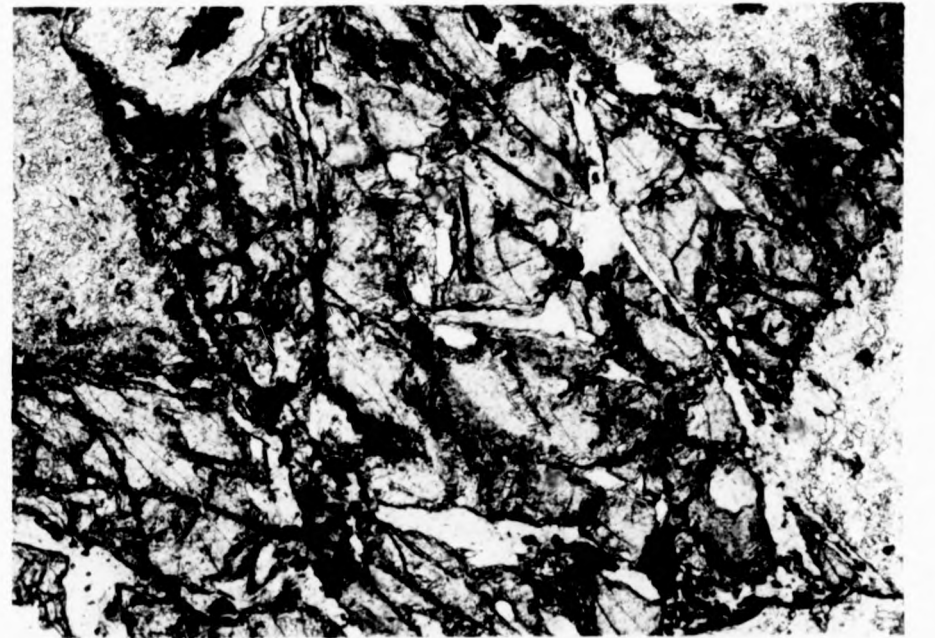


FIGURE 3.4.2. Pyroxene (dark grey) being replaced by chlorite (light grey) along fractures, sample 167K (Moel Siabod). PPL. X100.



actinolite amphibole or, rarely, chlorite. Almost all clinopyroxenes display some epitaxial amphibole overgrowth, however, it is rare for amphibole to replace the main pyroxene crystal (Figure 3.4.1). In contrast, when chlorite replaces pyroxene, replacement is frequently within the pyroxene crystal along cleavages and internal fractures (Figure 3.4.2).

ii) Plagioclase sites

The original igneous calcic plagioclase is now almost always variably albitised with only rare relict labradorite preserved. Several patterns of alteration can be distinguished within the plagioclase sites:- a) replacement of calcic plagioclase by albite, typically with some white mica (Figure 3.5.1), b) partial or total replacement of calcic plagioclase by chlorite (Figure 3.5.2), or, c), replacement of calcic plagioclase by albite and hydrous Ca/Al silicate minerals (Figure 3.5.3).

Typically alteration of calcic plagioclase is to albite plus one other secondary phase, or, occasionally, two other secondary phases, so that, for example, labradorite alters to albite + pumpellyite, albite + prehnite, or albite + pumpellyite + epidote.

iii) Olivine sites

Fresh olivine was never observed in the meta-dolerites of northern Snowdonia and its original presence can only be inferred from the occasional presence of chlorite pseudomorphs (Figure 3.1.4). These only occur in the more primitive samples displaying low  $FeO^*/MgO$  ratios. From the limited observations of unequivocal pseudomorphs after olivine, mainly from Cerrig Cochion and Tal-y-Fan, it would appear that olivine readily breaks down to chlorite. Only about 10% of the meta-dolerites

FIGURE 3.5.1. Twinned albitised plagioclase containing abundant white mica flakes, sample 167F (Moel Siabod). XP. X63.



FIGURE 3.5.2. Plagioclase (white) pervasively veined with chlorite (black), sample 73D (Cwm Eigiau). XP. X63.



FIGURE 3.5.3. i) (left) albitised plagioclase (light grey, low relief) in pyroxene (light grey, high relief) containing abundant pumpellyite (dark grey), sample N1 (north of Tal-y-Fan). PPL. X150.  
ii) (right) albitised plagioclase (white) containing abundant, anhedral pumpellyite (dark grey), sample 198C (Dolwyddelan). PPL. X63.



FIGURE 3.5.1. Twinned albitised plagioclase containing abundant white mica flakes, sample 167F (Moel Siabod). XP. X63.



FIGURE 3.5.2. Plagioclase (white) pervasively veined with chlorite (black), sample 73D (Cwm Eigiau). XP. X63.



FIGURE 3.5.3. i) (left) albitised plagioclase (light grey, low relief) in pyroxene (light grey, high relief) containing abundant pumpellyite (dark grey), sample N1 (north of Tal-y-Fan). PPL. X150.  
ii) (right) albitised plagioclase (white) containing abundant, anhedral pumpellyite (dark grey), sample 198C (Dolwyddelan). PPL. X63.



examined appear to have contained enough original olivine to be recognised after the effects of alteration to chlorite.

iv) Ore sites

In Section 3.2. it was shown that the ore phase consisted of a mixture of ilmenite and magnetite. The ilmenite is now largely altered to sphene whilst the magnetite appears to have remained relatively unaltered (Figure 3.1.2).

v) Interstitial sites

The interstitial sites are both interesting and problematical. Texturally they appear to reflect the alteration of interstitial, fine grained material, possibly formed during mesostasis. In some samples they account for as much as 20% of the rock.

Invariably these interstitial sites have been altered to chlorite frequently in association with other secondary phases such as epidote and actinolite (Figure 3.1.3) and more rarely, prehnite, pumpellyite or stilpnomelane (Figures 3.6.1 and 3.6.2).

In the far north of the Conwy Valley the chloritic interstitial sites also contain prehnite, pumpellyite and, occasionally, epidote. In addition, actinolite is only very rarely developed. Further south prehnite and pumpellyite are found only in the plagioclase sites. In these areas a frequent interstitial association is between chlorite, epidote (both optically pistacitic and clinzoisitic and often optically zoned) and fine needles of light green or colourless actinolite. In several samples brown stilpnomelane occurs associated with chlorite and epidote in the interstitial sites (Figure 3.6.2.).

Occasionally other mineral phases are found in the interstitial sites including pyroxene; brown amphibole and sphene, they are invariably



FIGURE 3.6.1. Interstitial alteration site containing chlorite (white, low relief), epidote (white, high relief) and abundant pumpellyite (medium grey), sample NIH. (north of Tal-y-Fan). PPL. X25.

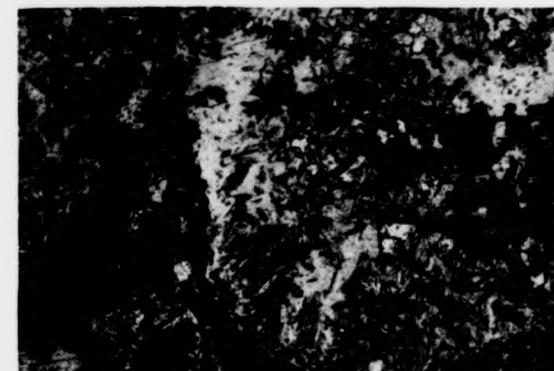


FIGURE 3.6.2. Interstitial alteration site containing chlorite (light grey), epidote (white) and stilpnomelane needles (black), sample 169R1 (Moel Siabod). PPL. X63.

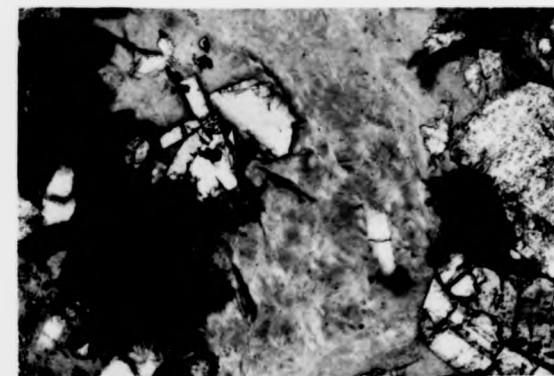


FIGURE 3.6.3. Interstitial alteration site containing acicular actinolite (white) nucleating on minute sphene crystals in chlorite (black), sample 168J (Moel Siabod). XP. X150.

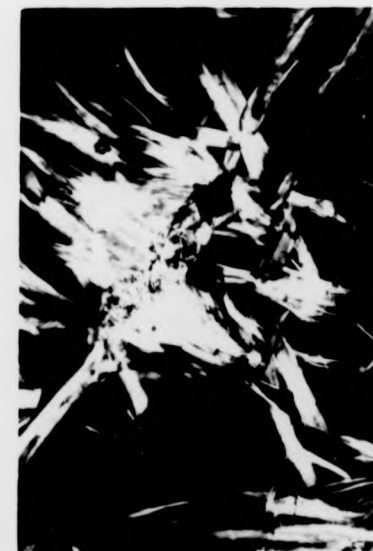


FIGURE 3.6.4. Interstitial alteration site containing acicular actinolite nucleating on a small brown amphibole crystal (darker grey) in a chloritic mass, sample 168J (Moel Siabod). PPL. X150.

FIGURE 3.6.1. Interstitial alteration site containing chlorite (white, low relief), epidote (white, high relief) and abundant pumpellyite (medium grey), sample NIH. (north of Tal-y-Fan). PPL. X25.

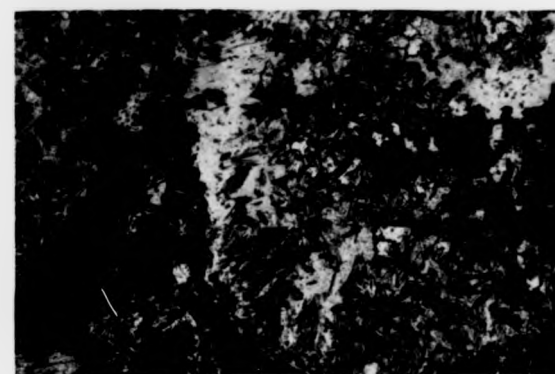


FIGURE 3.6.2. Interstitial alteration site containing chlorite (light grey), epidote (white) and stilpnomelane needles (black), sample 169R1 (Moel Siabod). PPL. X63.

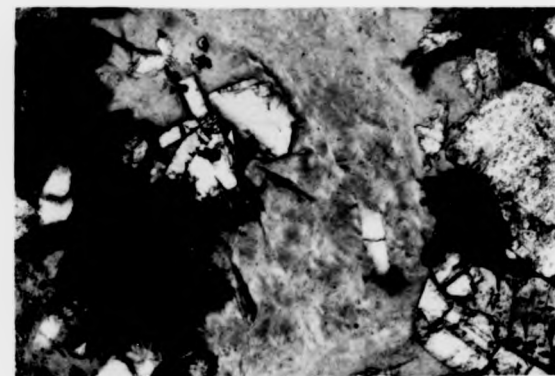


FIGURE 3.6.3. Interstitial alteration site containing acicular actinolite (white) nucleating on minute sphenes crystals in chlorite (black), sample 168J (Moel Siabod). XP. X150.

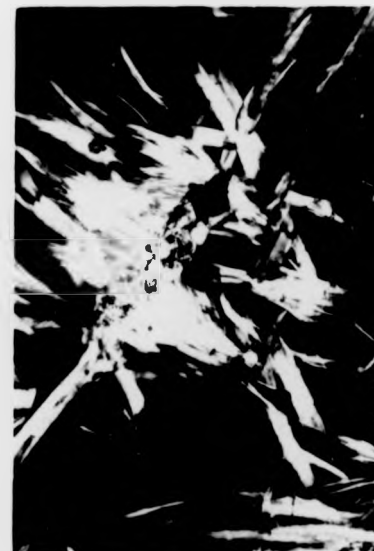


FIGURE 3.6.4. Interstitial alteration site containing acicular actinolite nucleating on a small brown amphibole crystal (darker grey) in a chloritic mass, sample 168J (Moel Siabod). PPL. X150.



FIGURE 3.6.1. Interstitial alteration site containing chlorite (white, low relief), epidote (white, high relief) and abundant pumpellyite (medium grey), sample N1H. (north of Tal-y-Fan). PPL. X25.

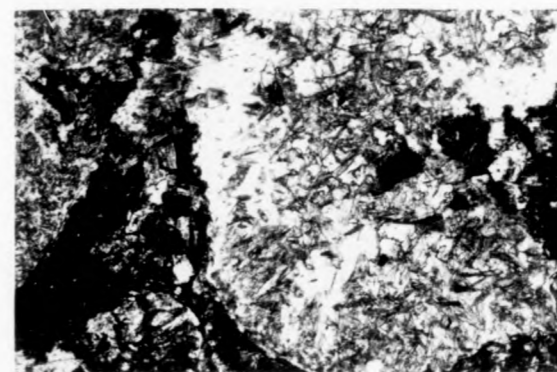


FIGURE 3.6.2. Interstitial alteration site containing chlorite (light grey), epidote (white) and stilpnomelane needles (black), sample 169R1 (Moel Siabod). PPL. X63.

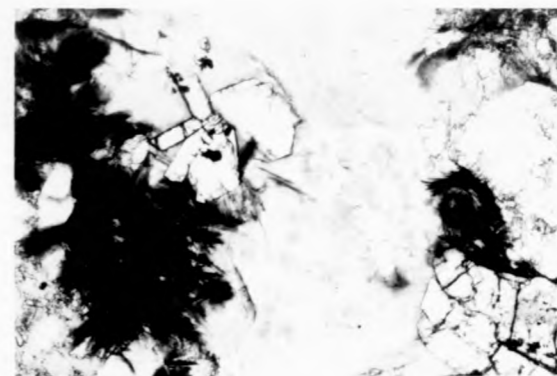
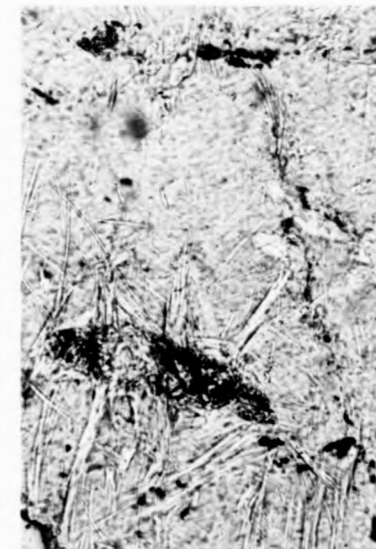


FIGURE 3.6.3. Interstitial alteration site containing acicular actinolite (white) nucleating on minute sphenes crystals in chlorite (black), sample 168J (Moel Siabod). XP. X150.



FIGURE 3.6.4. Interstitial alteration site containing acicular actinolite nucleating on a small brown amphibole crystal (darker grey) in a chloritic mass, sample 168J (Moel Siabod). PPL. X150.



very small. These small crystals often form the sites around which secondary phases, particularly needles of actinolite nucleate (Figures 3.6.3. and 3.6.4.). The preferential nucleation of secondary phases on these small crystals may occur because of the relatively large surface area. The presence of pyroxene and brown amphibole within the interstitial sites provides a further indication that these areas represent the products of mesostasis with the late magmatic pyroxene and amphibole crystals persisting as relict phases within a fine grained chloritic matrix.

### 3.6. Textural equilibrium

When attempting to assess equilibrium within a system it is important to define the scale over which evidence for equilibrium should be sought. Relevant to this discussion is the work of i) Boles and Coombs (1977), ii) Zen (1974), and iii) Kawachi (1975), who respectively argue that equilibrium should be investigated a) on the scale of a standard thin section, b) between phases no further than one millimeter apart, and c) between phases in actual physical contact. Clearly as the scale is reduced some approach towards equilibrium would be expected.

From the petrographic observations it is evident that disequilibrium exists on the scale of a thin section. This is most clearly shown through the presence of relict igneous phases, particularly clinopyroxene and, occasionally, labradoritic plagioclase. These minerals formed at temperatures far in excess of those prevalent during subsequent metamorphism but failed to fully react under the new pressure, temperature and fluid conditions.

The presence of optically zoned epidotes in many of the meta-dolerites, particularly those of Moel Siabod, again is indicative of

disequilibrium. Continuous zoning from coloured cores to colourless rims, such as that observed in northern Snowdonia, reflects the possible growth of epidote in the presence of a progressively less Fe-rich fluid. However, it is possible that the outer zone of the epidote is in equilibrium with the secondary mineral assemblage with the inner zones being effectively isolated from the metamorphic system. Closely related to this is the presence of more than one optically distinct type of a particular phase. In samples 148E and 168G, for example, pistatitic epidote occurs in the plagioclase sites and clinzoisitic epidote occurs in the interstitial sites.

Several samples contain secondary phases, usually prehnite, pumpellyite or epidote, that appear cloudy, contain fine inclusions or have spongy, diffuse margins, possibly indicating some mineral breakdown. Most of the samples displaying these features are from the relatively lower grade meta-dolerites of the northern Conwy Valley. These observations indicate that although disequilibrium exists, the system was slowly trending towards equilibrium, however, due to slow reaction rates, true textural equilibrium was never fully attained.

Finally, the phase rule can be applied, with caution, to low-grade metamorphic rocks (Bevins, 1979; Bevins and Rowbotham, 1983). The presence of relict igneous phases is a complication as only part of the system can be involved in metamorphism, hence the components locked in any unaltered phases cannot be involved in the production of the secondary assemblage, Jolly (1970). If albite, quartz, calcite, sphene, white mica and fluid are assumed to account for  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{CO}_2$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$  and  $\text{H}_2\text{O}$  respectively, the system can be represented on a tetrahedral  $\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{FMO}$  ( $\text{FeO}$ ,  $\text{MgO}$ ) -  $\text{CaO}$  plot (Hashimoto, 1972) which allows four out of the five phases chlorite, actinolite, epidote, prehnite and pumpellyite to coexist. From Appendix 4 it can be seen

that 92% of the samples contain four (or less) of these phases and do not, therefore, violate the phase rule. The remaining 8%, however, do violate the phase rule as they contain all five phases. Most of the samples included in this latter group are from the northern Conwy Valley and display other evidence for disequilibrium such as the breakdown and clouding of minerals. Clearly, therefore, on the thin section scale application of the phase rule indicates a degree of disequilibrium.

Application of the phase rule to mineral sub-assemblages developed within individual alteration sites (Section 3.5), indicates equilibrium both within and between similar alteration sites on the thin section scale with disequilibrium occurring only between the mineral sub-assemblages developed in different alteration sites. For example, in Sample 66H the typical sub-assemblage of the interstitial sites is chlorite + epidote + actinolite whilst that of the plagioclase sites is chlorite + pumpellyite + prehnite (with the prehnite showing some evidence of instability). Clearly these sub-assemblages are distinct. Hence only a part of the thin section can be viewed as displaying equilibrium or disequilibrium related not to scale but more to the specific site of alteration. This factor could account for some of the regional and local variability in secondary mineral assemblages apparent within northern Snowdonia.

### 3.7. The relationship between major element geochemistry and petrography

#### 3.7.1. Geochemical/petrographic responses to metamorphism

From the major element geochemical analyses of Chapter 2 and the petrographic observations of this Chapter three distinct geochemical/petrographic responses to metamorphism can be recognised:-

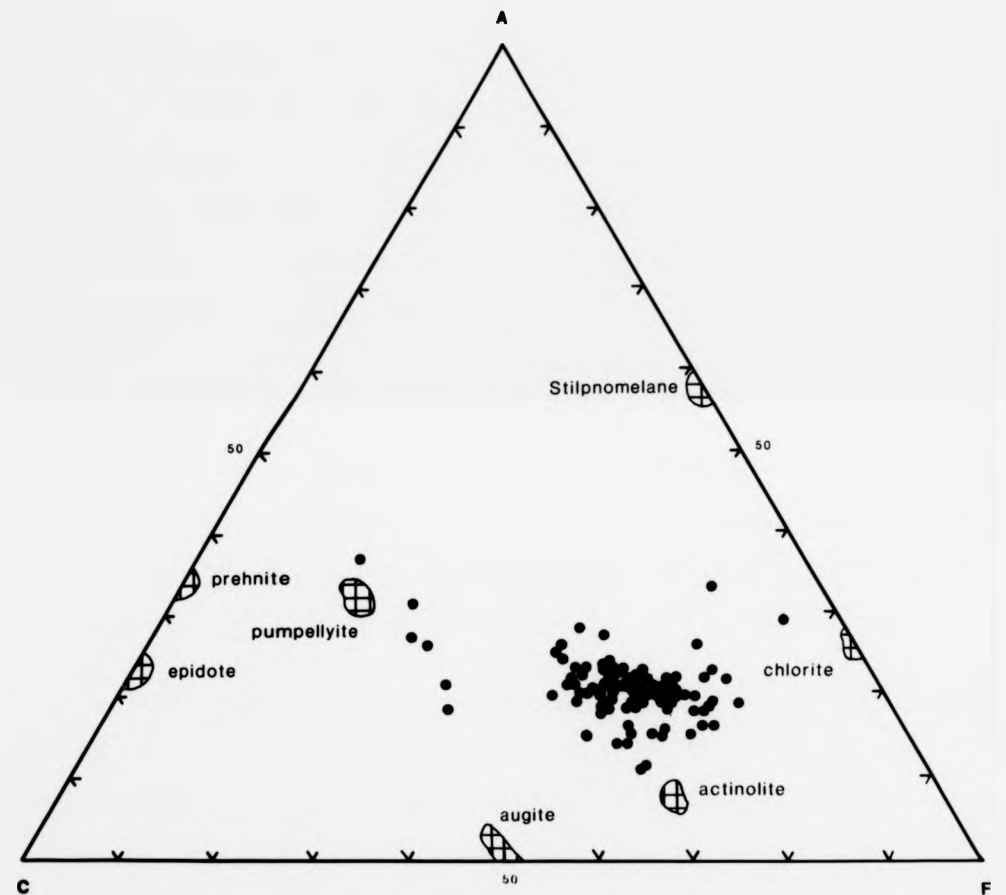
- i) elements that have remained immobile because they have been retained in refractory phases, for example, P in apatite.

ii) elements that have remained essentially immobile on the hand specimen scale. Elements displaying this type of response include  $TiO_2$ ,  $MnO$ ,  $FeO^*$ ,  $MgO$  and  $Al_2O_3$ . Although primary mineral breakdown has resulted in element release, crystallisation of new phases has resulted in the reincorporation of these elements in new phases at, or close to, the site of alteration. Specific examples include the retention of Ti as ilmenite is replaced by sphene and the release of Fe and Mg from olivine or pyroxene with subsequent reincorporation in the chlorite with which they are replaced

iii) elements that have been released during metamorphism and have been only partially reincorporated in locally developed secondary phases, resulting in, either, local element mobility between different parts of an intrusion, or (potentially) regional element mobility out of an intrusion. Elements displaying this sort of response include  $CaO$ ,  $Na_2O$ , and  $SiO_2$ .

The most obvious example of this kind of response is that displayed by Ca which is clearly depleted in many meta-dolerite samples and enhanced in others. This might indicate that Ca released during feldspar and pyroxene breakdown is only partially reincorporated in secondary phases at or near the site of alteration. Excess Ca enters the fluid and is subsequently precipitated to produce epidote rich samples enriched in Ca (for example, Samples 85B, 85C, 169R1 and 148C). This trend can be clearly seen in the ACF diagram (Figure 3.7) with the majority of samples displaying a varying degree of relative Ca depletion but with a number of samples clearly displaying marked Ca enrichment (relative to fresh basalts). If significant Ca had left the meta-dolerites some evidence might be expected through Ca mineralisation in the surrounding country rocks. No such epidote or calcite mineralisation is observed in northern Snowdonia indicating that little Ca has left the

FIGURE 3.7. ACF ( $A = Al_2O_3 + Fe_2O_3 - Na_2O - K_2O$ ,  $C = CaO - 3P_2O_5$ , and  $F = FeO + MgO + MnO$ ) for the meta-dolerites from the Conwy Valley. Also shown are the compositional fields for prehnite, epidote, pumpellyite, augite, actinolite, chlorite and stilpnomelane.





intrusions.

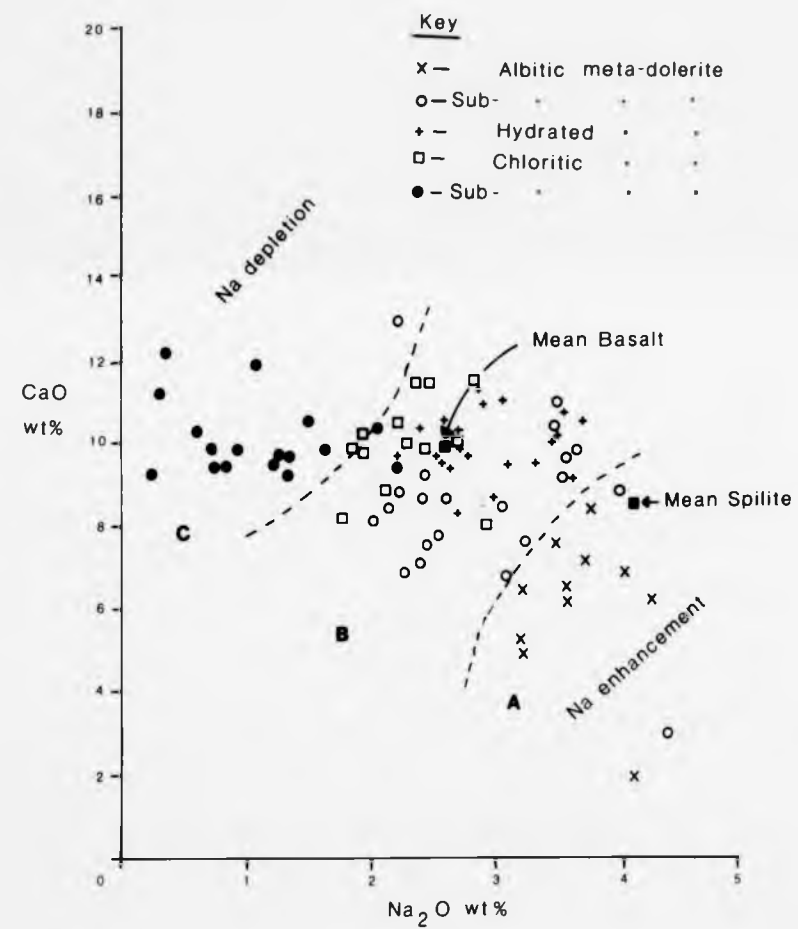
It would also appear that Na behaves in a similar fashion to Ca on the hand specimen scale, with samples displaying a range of Na values from extreme depletion to marked enhancement (relative to fresh tholeiitic basalts). Figure 3.8. shows that much of this variation in Na can be attributed to the breakdown of an originally calcic plagioclase to dominantly albite (relative Na enrichment), albite and secondary hydrous phases, or chlorite (relative Na depletion). The different types of alteration possibly reflect original differences between intrusions and, particularly, between samples (Section 3.7.2).

#### 3.7.2. Geochemistry and the bulk alteration characteristics

In Section 3.3.1. four types of meta-dolerite were recognised based on the abundance of albite, chlorite and epidote. A representative major element geochemical analysis for a sample of each of the meta-dolerite types is presented in Table 3.A.

Primary magmatic differences between the dolerites can be examined through the distribution of elements such as  $TiO_2$ ,  $FeO^*$ ,  $P_2O_5$  and the  $FeO^*/MgO$  ratio (Chapter 2). From Table 3.A. it would appear that a systematic relationship exists between primary geochemistry and alteration characteristics with the chlorite rich sample displaying relatively low  $TiO_2$ ,  $P_2O_5$  and  $FeO^*/MgO$  ratio, the albite rich sample displaying relatively high  $TiO_2$ ,  $P_2O_5$ , and  $FeO^*/MgO$  ratio and the hydrated sample displaying intermediate geochemical characteristics. The implication of this observation is that the albite and chlorite rich samples represent relatively more and less fractionated primary dolerite respectively, so that original differences in the degree of fractionation have influenced the nature of subsequent alteration. The bulk alteration characteristics are plotted against the  $FeO^*/MgO$  differentiation index

FIGURE 3.8. CaO vs Na<sub>2</sub>O and the alteration characteristics of the Conwy Valley meta-dolerites.

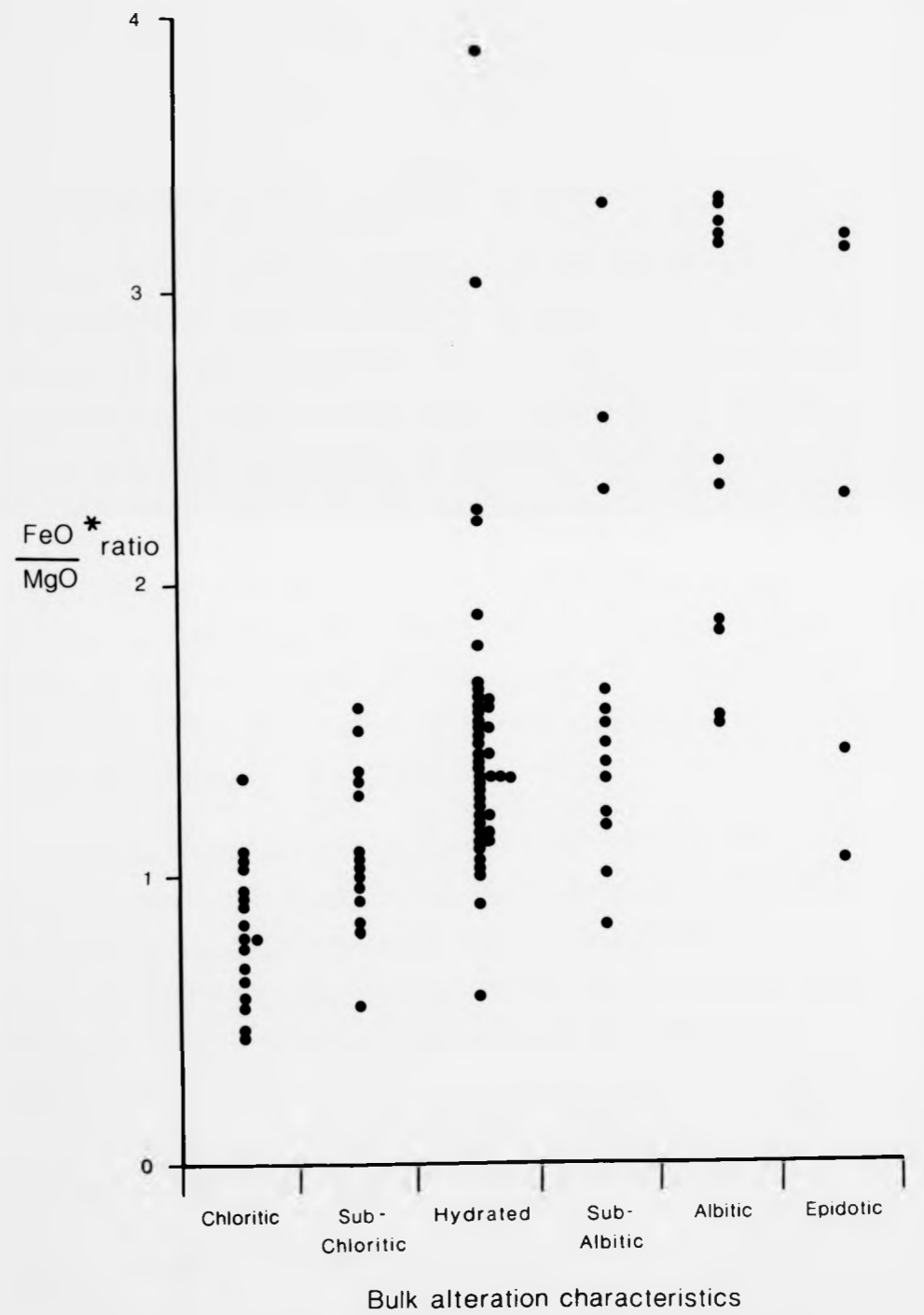


Type of meta-dolerite alteration

element oxide	Chlorite rich sample (Sample 66A)	Typical hydrated sample (Sample 168D)	Albite rich sample (Sample 179C)	Epidote rich sample (Sample 148C)
SiO <sub>2</sub>	44.54	48.88	53.43	46.58
TiO <sub>2</sub>	0.69	1.56	2.04	1.31
Al <sub>2</sub> O <sub>3</sub>	12.65	15.29	13.80	14.42
Fe <sub>2</sub> O <sub>3</sub>	2.58	1.74	7.58	3.50
FeO	6.14	7.00	6.20	4.49
MnO	0.16	0.18	0.25	0.16
MgO	18.07	8.48	3.41	7.18
CaO	9.22	9.60	3.02	19.31
Na <sub>2</sub> O	0.27	3.58	4.41	n.d.
K <sub>2</sub> O	0.38	0.35	0.43	0.22
P <sub>2</sub> O <sub>5</sub>	0.02	0.10	0.66	0.19
H <sub>2</sub> O	5.69	3.58	3.71	4.03
FeO*/MgO ratio	0.47	1.01	3.82	1.06

TABLE 3.A. Representative geochemical analyses of a chlorite rich, hydrated, albite rich and epidote rich meta-dolerite sample.

FIGURE 3.9. Meta-dolerite alteration characteristics vs the FeO\*/MgO ratio.



in Figure 3.9. where broad correlation appears to exist. The general relationships of Figure 3.9. are:-

FeO\*/MgO ratio < 1.0 - chlorite rich samples.

FeO\*/MgO ratio 1.0 - 2.0 - hydrated samples.

FeO\*/MgO ratio > 2.0 - albite rich samples.

No systematic relationship exists between the FeO\*/MgO ratio and the development of epidote rich samples. In Table 3.A. the geochemical characteristics of the epidote rich sample are very similar to those of the hydrated meta-dolerite sample, again indicating that there is no primary geochemical control on the development of epidote rich samples.

The relative geochemical effects of different types of alteration can be seen through the distribution of the more mobile elements in Table 3.A. particularly elements such as Na<sub>2</sub>O and CaO. The clearest example of the influence of metamorphism on geochemistry occurs in the epidote rich sample where there has been extreme CaO enrichment relative to the other samples.

It would appear that differences in the composition of the original dolerite, reflecting variable fractionation, have influenced the nature of subsequent alteration with the more fractionated samples altering to albite rich meta-dolerites and the less fractionated samples altering to chlorite rich meta-dolerites (relative to the typical hydrated meta-dolerite). Epidote rich meta-dolerites develop where there has been significant enrichment of Ca during metamorphism and their development is not related to primary compositional control.

### 3.7.3. Geochemistry and specific mineral phases

In addition to the relationships outlined above, two specific geochemical - mineralogical associations exist; i) an association

between the presence of stilpnomelane and high  $FeO^*/MgO$  ratios (for example, in Samples N1G, N1K, 141C, 141D, 85B, 168R1 and 179C). The development of stilpnomelane in more fractionated rocks was originally described by Kawachi (1975). More recently Bevins and Rowbotham (1983) have drawn attention to this relationship in metamorphosed, fractionated, basic and intermediate rocks from Wales, and, ii) an association between low  $FeO^*/MgO$  ratio and the presence of chlorite pseudomorphing after olivine. This relationship reflects the removal of olivine from the magma at an early stage, hence its presence in only the least fractionated samples more especially from Cerrig Cochion and Tal-y-Fan.

From the above discussion it is clear that stilpnomelane occurs preferentially in the albite rich meta-dolerite samples and chlorite pseudomorphs after olivine in the chlorite rich meta-dolerite samples representing the most and least fractionated samples respectively.

### 3.8. Discussion

#### 3.8.1. Bulk alteration characteristics

Comparison of the meta-dolerites from the Conwy Valley and low grade alteration of basic rocks in other areas reveal several interesting similarities. Figures 3.10.1. and 3.10.2. are ACF diagrams taken from Smith (1968) and Cann (1969), respectively, and demonstrate the chemical variation observed in "altered basic lavas", and "spilitised basalts". The "orthospilite", "bulk pillow lava" and "hayalospilite" (Cann, 1969), and the "spilitic trend" (Smith, 1968) appear to correspond to the albite rich, hydrated and chlorite rich meta-dolerite samples of northern Snowdonia, whilst the trend of Smith (1968) towards "dimineralic assemblages" corresponds to the Ca enriched, epidote rich samples of northern Snowdonia. Cann (1969) relates these trends to differential alteration between the more primitive, glassy, pillow rims and less

FIGURE 3.10.1. ACF diagram from Smith (1968) showing a spilitic and a dimineralic alteration trend.

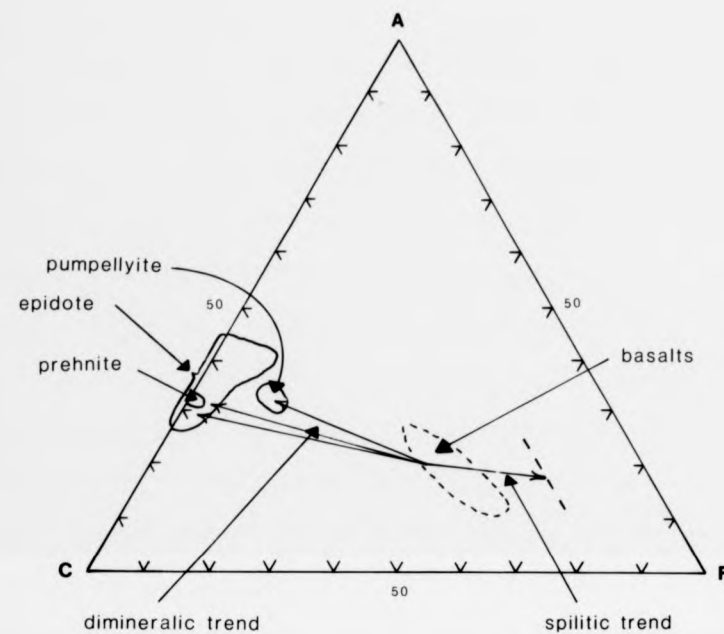
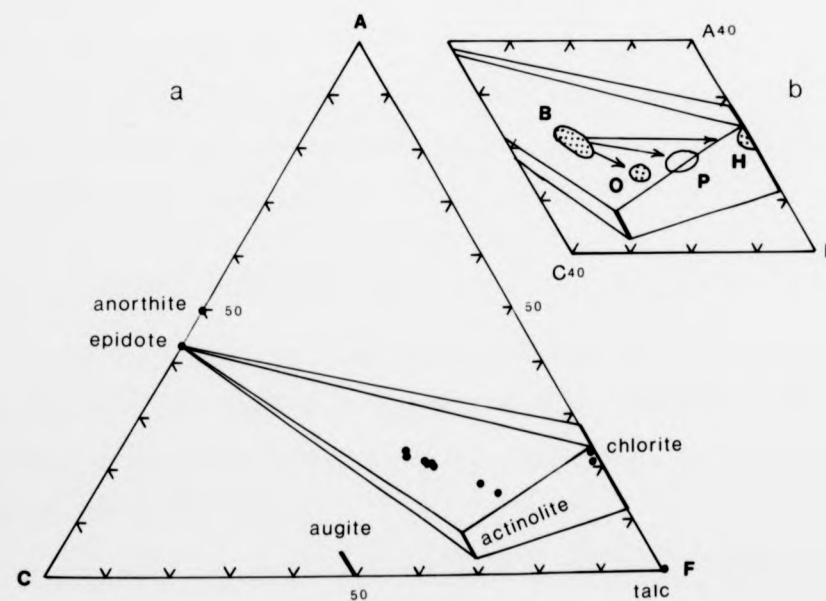


FIGURE 3.10.2. ACF diagram from Cann (1969) showing the effects of spilitisation on an original basalt (B).  
 O = orthospilite, P = bulk pillow lava, H = hayalospilite.



primitive, crystalline, pillow cores.

The dimineralic trend is typified by extreme local enrichment of CaO and has been frequently observed in low/medium grade, metamorphosed basic rocks, (Smith, 1968; Miyashiro et al., 1971; Humphris and Thompson, 1978) but remains a problem in that there appears to be no simple correlation between original chemistry and alteration. Miyashiro et al. (1971) relate the sporadic development of epidote rich domains to locally high oxygen pressures indicated by high  $H_2O$  contents and  $Fe_2O_3/FeO$  ratios. Local variation in oxygen pressure could be governed by factors such as fracturing, jointing, permeability of the system, fluid chemistry, etc. In northern Snowdonia no clear relationship between the development of epidote rich meta-dolerite samples and features such as jointing and fracturing was observed. However, all the epidote rich samples occur well inside the meta-dolerite sills and display sharp contacts with the surrounding, more characteristic, hydrated meta-dolerites. It is possible that the epidote in these samples has preferentially nucleated beneath relatively less permeable layers within the intrusions.

### 3.8.2. The nature of metamorphism

In Section 3.6. it was shown that on the thin section scale a large degree of petrographic disequilibrium exists within the meta-dolerites, particularly between mineral sub-assemblages developed in different alteration sites.

If secondary mineral sub-assemblages from specific alteration sites are considered the complex petrographic pattern apparent within northern Snowdonia can be simplified. Prehnite and pumpellyite occupy both the interstitial and plagioclase sites only in the far north of the Conwy Valley, any prehnite or pumpellyite identified from the central and



southern Conwy Valley occurs only in the plagioclase sites. Clearly the microchemical environment of the interstitial sites is suitable for prehnite and pumpellyite development so that it is possible that the metamorphic conditions were such that south of Tal-y-Fan prehnite and pumpellyite either only formed in the plagioclase sites, or formed in the interstitial sites but were subsequently replaced by the higher grade, chlorite + epidote + actinolite sub-assembly. Secondary mineral assemblages defined on the basis of observations on a whole thin section may be misleading in that petrographic disequilibrium frequently occurs at this scale. It would appear, therefore, that a more realistic approach in low-grade metamorphic rocks is to examine secondary mineral sub-assemblages developed within specific alteration sites rather than the total mineral assemblage displayed by the whole thin section (Jolly, 1970). This type of approach is considered normal when investigating, for example, the incipient metamorphism of clastic sediments where the cement material has preferentially responded to increased pressures and temperatures (Kisch, 1983a).

From the petrographic observations and the above discussion some tentative suggestions concerning metamorphic conditions can be made. The far north of the Conwy Valley appears to have experienced generally lower grade conditions than the rest of northern Snowdonia, probably within the prehnite-pumpellyite facies. Further south there is often conflicting petrographic evidence reflecting contrasting secondary mineral sub-assemblages developed in different alteration sites. The occasional presence of a lower grade pumpellyite bearing sub-assembly in the plagioclase sites and the frequent occurrence of the higher grade actinolite bearing sub-assembly in the interstitial sites might indicate that two phases of metamorphism are recorded. The presence of "relict" lower grade sub-assemblages in the plagioclase sites might

reflect slower reaction rates within these sites (relative to the interstitial sites). The two apparent phases of metamorphism could reflect different stages of the same general metamorphic event with the plagioclase site sub-assemblage simply reflecting an earlier stage, and the interstitial site sub-assemblage a later stage, of a continuous prograde metamorphic event. This interpretation might be supported by the presence of numerous continuously zoned epidotes in the interstitial sites and the presence of amphibole needles overgrowing chlorite and epidote within the interstitial sites.

Further discussion of the petrographic observations is withheld until the next chapter where the petrographic data is quantitatively supported by secondary phase compositional data.

### 3.9. Concluding remarks

From the detailed observations, of secondary mineral assemblages and the nature of alteration, on 190 meta-dolerites from northern Snowdonia several conclusions can be tentatively drawn.

The primary mineralogy of the meta-dolerites appears to have been augitic pyroxene + labradoritic plagioclase + ilmenite/magnetite ± olivine. In addition, all samples contain interstitial areas that are now largely chloritised and probably represent the products of late magmatic crystallisation.

The general alteration characteristics of the meta-dolerites appear, in part, to reflect the original composition of the dolerites with the least fractionated samples being characteristically chlorite rich and the most fractionated being albite rich. Epidote rich samples do not appear to reflect original chemical differences, rather the effects of local Ca enrichment within the dolerites during low-grade metamorphism.

Regional and local variation in secondary mineral assemblages is marked. Lower grade (prehnite bearing) assemblages are concentrated in the northern Conwy Valley with higher grade (actinolite bearing) assemblages being concentrated in the central and southern Conwy Valley and central northern Snowdonia. A significant increase in the amount of pumpellyite present in the far south of the Conwy Valley might indicate slightly lower grade, relative to the central Conwy Valley.

Extensive petrographic disequilibrium on the thin section scale suggests that the concept of equilibrium, as applied to high-grade metamorphic rocks, is inappropriate for low-grade rocks. Equilibrium appears to occur between similar alteration sites within a thin section, but not necessarily between the different types of alteration site. This inter-alteration site variation in sub-assemblages is thought to reflect the slow reaction rates at these low grades and might be related to the preferential passage of fluid through interstitial sites and the increased susceptibility of microcrystalline interstitial material to the processes of alteration.

## CHAPTER 4

### MINERAL FORM AND CHEMISTRY

#### 4.1. Introduction

Electron microprobe analysis of the mineral chemistry has been undertaken on 17 samples from the Conwy Valley. As far as possible all mineral phases present within a sample have been analysed. However, occasionally phases were present only as isolated small grains which proved impossible to probe. Analyses were performed on a Geoscan Mk II or a Cameca (Camebax) electron microprobe at the University of Manchester and a Geoscan II electron microprobe at the University of Cambridge.

All but one of the 17 samples are from the Conwy Valley meta-dolerites, the exception being a sample of pegmatitic diorite from the Penmaenmawr intrusion. Criteria governing sample selection included: i) geographical distribution - samples were chosen to provide representative cover throughout the Conwy Valley in order to investigate any systematic variation in mineral chemistry within the Valley, ii) the presence of petrographically interesting secondary mineral assemblages and features such as zoning, optical variation within individual secondary phases, mineral reactions, etc., and iii) the availability of bulk rock geochemical data in order that the effects of host rock composition on secondary mineral chemistry can be precisely quantified. The 16 meta-dolerites all have major element geochemical data available, the Penmaenmawr diorite lacks geochemical control. Sample locations are listed in Appendix 2 (i).

The aims of the mineral chemistry analysis include:-

i) critical analytical assessment of the petrographic observations, such as the quantification of the frequently observed zonation in epidote, precise chemical differences between optically different epidotes in

contrasting alteration sites, chemical differences between epitaxial amphiboles and acicular amphiboles nucleating away from clinopyroxenes.

ii) Determination of any systematic chemical variation in specific minerals between samples from different parts of the Conwy Valley. This data can then be used together with the geochemical analysis in an attempt to assess the importance of bulk rock chemistry in controlling mineral chemistry.

iii) An assessment of any approach towards chemical equilibrium in the meta-dolerites.

iv) Use of the mineral chemical data and petrography to determine the parameters and history of metamorphism in northern Snowdonia.

v) Use of the clinopyroxene data to determine the magmatic affinities of the fresh dolerites.

#### 4.2. Relict igneous phases

##### 4.2.1. Clinopyroxenes

A total of 65 analyses have been obtained from the 16 meta-dolerite samples (16 clinopyroxene analyses are presented in Appendix 5). Clinopyroxene recalculations are on the basis of 6 oxygens in a general formula of  $X_{1-P} Y_{1+P} Z_2 O_6$ ; where  $X = Ca$  and  $Na$ ,  $Y = Mg, Fe^{2+}, Fe^{3+}, Al^{VI}$  and  $Ti$ ,  $Z = Si$  and  $Al^{IV}$  and  $P = 0-1$  (Deer et al., 1962). Tetrahedral sites are filled with  $Si$  and  $Al$ , excess  $Al$  is allocated to the octahedral sites. The clinopyroxenes are plotted on a  $Di - Hd - En - Fs$  compositional diagram (Figure 4.1). Most of the clinopyroxenes fall within the augitic field of Poldervaart and Hess (1957). It is clear that little chemical variation exists within the clinopyroxenes of the Conwy Valley. The main variation is in  $Mg$  and  $Fe$  with clinopyroxenes from samples 169R3, N1k and T13 being relatively  $Fe$ -rich compared to

FIGURE 4.1. Composition of clinopyroxenes from the Conwy Valley on the Di - Hd - En - Fs diagram of Poldervaart and Hess (1957).

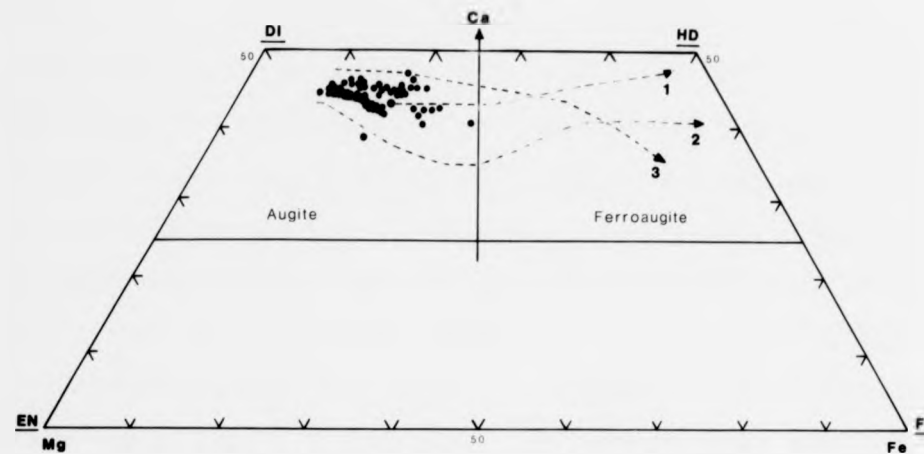
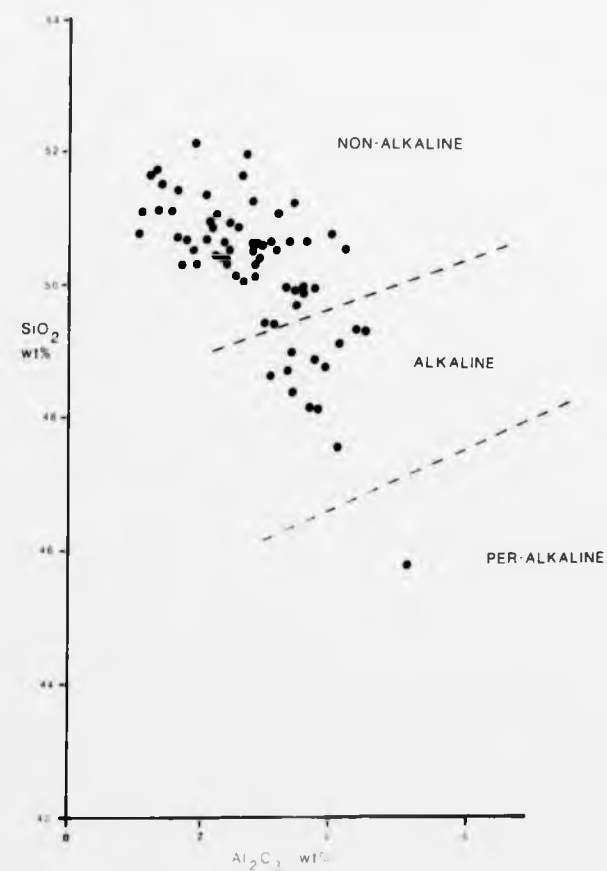


FIGURE 4.2.  $Al_2O_3$  vs  $SiO_2$  for clinopyroxenes from the Conwy Valley. Non-alkaline, alkaline and per-alkaline fields from Le Bas (1962).



those from other samples. This variation is thought to reflect differences in the degree of fractionation with the more Fe-rich clinopyroxenes occurring in the more differentiated dolerites. The compositional trends for pyroxenes from the Skaergaard intrusion, Shiant Isles Sill and Shonkin Sag laccolith reflecting a tholeiite intrusion, a moderately undersaturated intrusion and a strongly undersaturated alkaline intrusion, respectively, are also shown. Many of the Mg-rich clinopyroxenes appear to cluster close to the Shiant Isles trend. There is no consistent Ca depletion with fractionation typical of the Skaergaard trend and similar to that observed in the Llanwnda intrusion, South Wales (Bevins, 1979). The Conwy Valley clinopyroxene compositions are very similar to those from Y Garn, Llech Dafad and Tresessylt, South Wales (Bevins, 1979), displaying slight Ca depletion with fractionation and taken to reflect equilibrium crystallisation of clinopyroxene from a tholeiitic parent magma.

Le Bas (1962) used clinopyroxene compositions to determine magmatic affinity. In Figure 4.2. the Conwy Valley clinopyroxenes are plotted on a  $\text{SiO}_2 - \text{Al}_2\text{O}_3$  discrimination diagram. Clearly there is marked variation, however, the overall distribution is consistent with clinopyroxene precipitation from a non-alkaline parental magma as over 80% of the analyses fall in the non-alkaline field of Le Bas.

#### 4.2.2. Plagioclase feldspar

Most of the plagioclase feldspar in the Conwy Valley has suffered extensive albitisation. However, plagioclase feldspar from samples 66A and 66I yield labradoritic compositions ( $\text{An}_{49-59}$ ). These analyses are thought to reflect the composition of the original igneous feldspar crystallised in equilibrium with the augitic pyroxene. The remaining plagioclase analyses all yield low An contents ( $\text{An}_{0-25}$ ) reflecting the

effects of variable metamorphic albitisation. These feldspars are discussed more fully in Section 4.3.9.

The remaining primary constituents (ore, olivine and the interstitial products of mesostasis) are all pervasively altered (Section 3.2).

The relict igneous phase chemistry supports the geochemically deduced conclusion that the meta-dolerites of the Conwy Valley represent metamorphosed, variably differentiated tholeiitic sills.

#### 4.3. Secondary phases

##### 4.3.1. Pumpellyite

Pumpellyite has been recognised in 65 samples of meta-dolerite from northern Snowdonia (Figure 4.3.1). A variety of characteristic pumpellyite forms have been recognised including:-

- i) discrete minute needle or lathlike crystals of anhedral masses developed within albitised plagioclase feldspar.
- ii) isolated minute crystals in the groundmass associated with chlorite, albite and epidote.
- iii) relatively large (0.1 mm) subhedral or euhedral crystals in the interstitial alteration sites often associated with chlorite and epidote.
- iv) large (0.3 mm) subhedral crystals associated with prehnite and epidote in the Penmaenmawr diorite intrusion.
- v) small isolated radiating "wheels" of dark green crystals.

Of these only i - iii are frequently observed, iv and v being restricted to a single intrusion (the Penmaenmawr diorite) and a single sample (T13) respectively.

Optically the pumpellyites are distinctive although rather variable.



FIGURE 4.3.1. Pod of pumpellyite crystals (green) in the Penmaenmawr meta-diorite, sample 35G. PPL. X35.



FIGURE 4.3.2. Large fan of prehnite, displaying second order birefringence colours, within the Penmaenmawr meta-diorite, sample 35G. XP. X35.

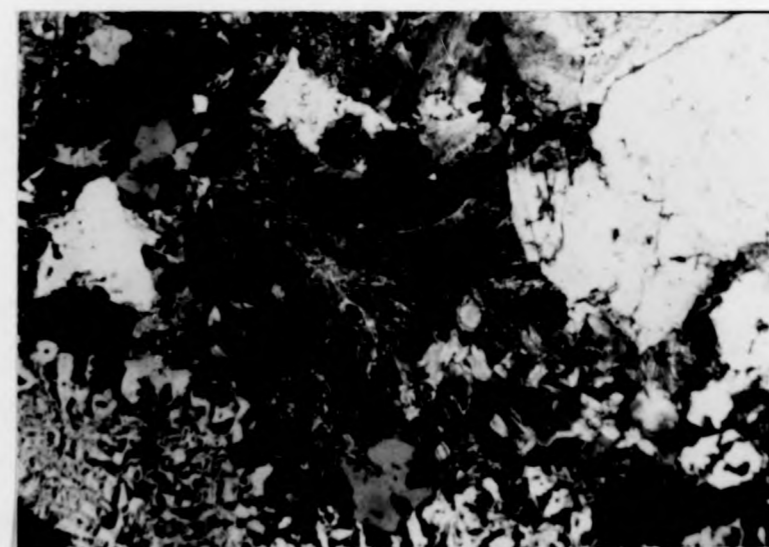


FIGURE 4.3.1

Pod of pumpellyite crystals (green) in the Penmaenmawr meta-diorite, sample 35G. PPL. X35.

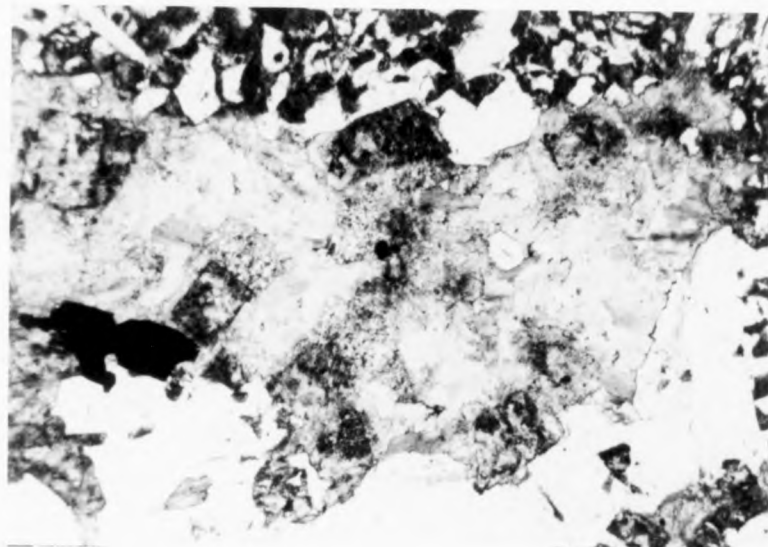
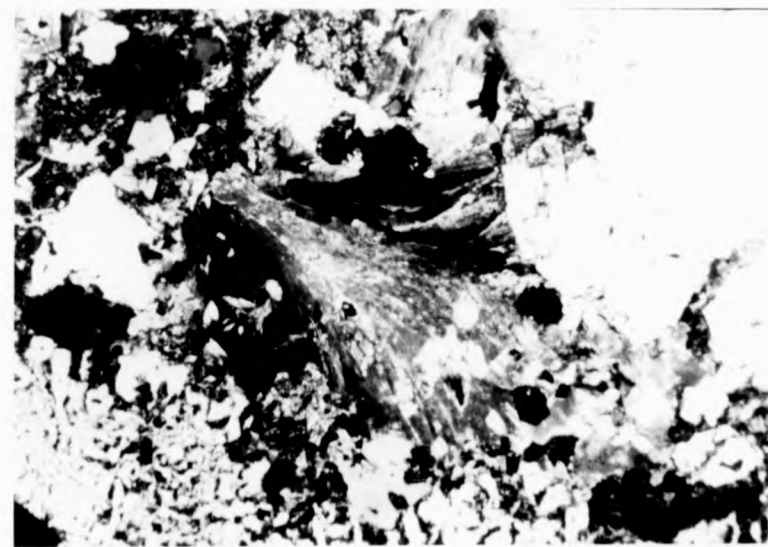
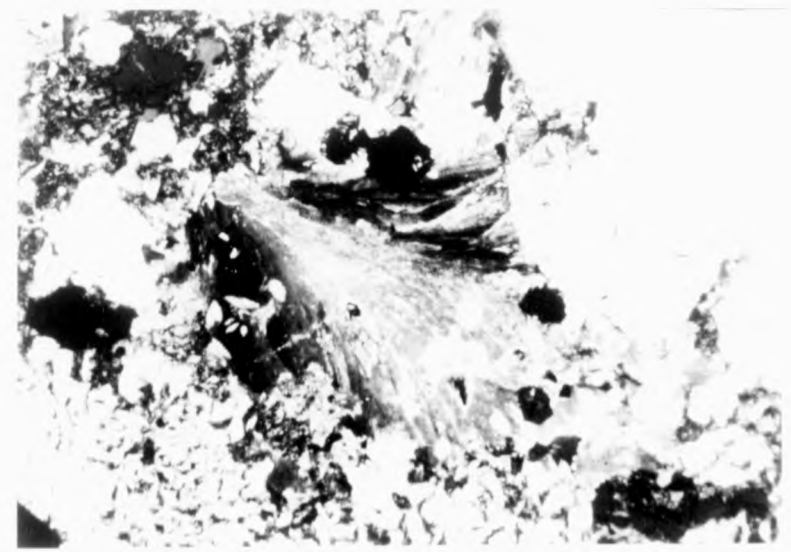
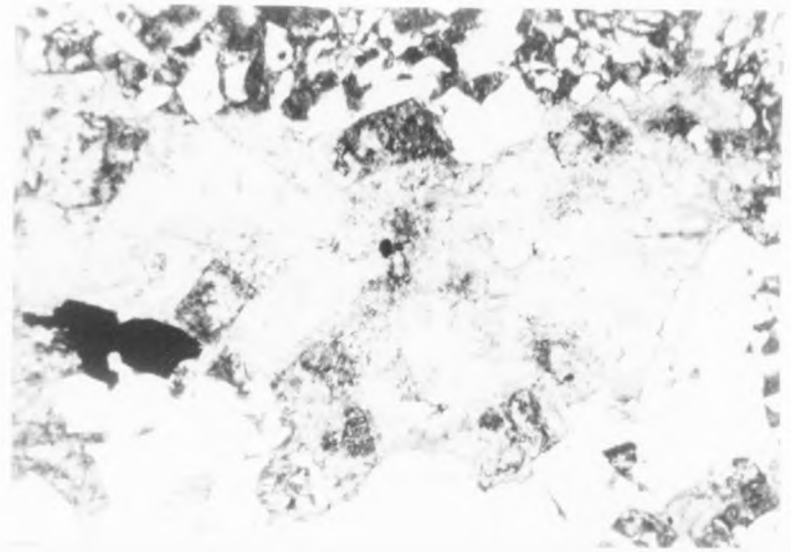


FIGURE 4.3.2

Large fan of prehnite, displaying second order birefringence colours, within the Penmaenmawr meta-diorite, sample 35G. XP. X35.





Most frequently pumpellyites are light to dark green in colour and display marked pleochroism with  $\alpha$  = pale green,  $\beta$  = green and  $\gamma$  = colourless, occasionally the  $\beta$  pleochroic colour is a blue-green. In the southern Conwy Valley distinctive yellow/fawn pumpellyite occasionally occurs (with  $\alpha$  = pale yellow,  $\beta$  = yellow/fawn and  $\gamma$  = colourless) together with the more typical green pumpellyite. No colourless pumpellyite has been recognised in northern Snowdonia. Interference colours are invariably anomalous giving varieties of crimson and deep blue.

Pumpellyite colour is related to composition, particularly Fe content, with a progressive decrease in colour intensity as Al/Fe increases (Coombs, 1953; Surdam, 1969; Coombs et al., 1976). Where pumpellyites of different forms are present no systematic differences in optical properties are apparent. In sample 168G, where green and yellow pumpellyites coexist, they both occur as spongy masses in albitised plagioclase feldspars.

There have been 54 pumpellyite analyses obtained from 10 samples taken throughout the Conwy Valley (24 analyses are presented in Appendix 5). Pumpellyite recalculations are after Coombs et al. (1976) who use a pumpellyite formula of  $W_4 X_2 Y_4 Z_6 O_{(20+x)} OH_{(8-x)}$ ; where W = Ca and Mn,  $X = (Mg, Fe^{2+}, Mn)_{2-x}$ ,  $(Fe^{3+}, Al)_x$ ,  $Y = Fe^{3+}$  and Al, and  $Z = Si (+Al)$ .

Manganese was detected in only 4 of the analyses. The oxidation state of iron is unknown, recalculation assumes that all iron is ferrous. Passaglia and Gottardi (1973), using wet chemical analysis, show that  $(Mg + Fe^{2+} + Mn)$  in the X sites typically varies between 0.71 and 1.55 (the remaining X sites being occupied by Al). In the Conwy Valley pumpellyites  $(Mg + Fe^{2+} + Mn)$  ranges from 1.08 - 1.91 implying that significant but highly variable amounts of  $Fe^{3+}$  occur, presumably

substituting for Al in the X (and Y) sites. Surdam (1969) describes  $\text{Fe}^{3+}$  bearing pumpellyites from Vancouver Island and relates the high  $\text{Fe}^{3+}$  content to low confining pressures. At high confining pressures  $\text{Fe}^{3+}$  preferentially enters coexisting stilpnomelane, epidote or chlorite. Schiffman and Liou (1980) show that high pressures favour the development of Al-rich pumpellyite and low pressures favour the development of Fe-rich pumpellyite.

Within the Conwy Valley pumpellyites, marked variation exists in Al, Fe and Mg both between analyses from the same sample and between samples. Intra-crystal variation in composition was not rigorously examined because most of the pumpellyite crystals are very small and numerous analyses on a single crystal were not practicable. The variation in pumpellyite chemistry within a sample does not appear to be systematic and is not related to differences in mode of occurrence, mineral form or site of alteration. The chemical variation displayed by pumpellyites from the Conwy Valley is clearly seen in Figures 4.4.1. and 4.4.2. where  $\text{FeO}^*$  (total iron as FeO) is plotted against  $\text{Al}_2\text{O}_3$  for individual analyses and bulk intrusion data respectively. Also shown are the pumpellyite compositional fields from Vancouver Island (Surdam, 1969), Upper Wakatipu (Kawachi, 1975) and Loeche (Coombs et al., 1976). The Conwy Valley pumpellyites fall into two distinct groups, those from the meta-dolerites and those from the Penmaenmawr intrusion. Within the meta-dolerite pumpellyites there does appear to be a small increase in Fe content from south to north in the Conwy Valley with one exception being pumpellyite from the Moel Ddefaid intrusion. The more Fe-rich pumpellyites from the Penmaenmawr intrusion may be either a continuation of this trend or reflect the unique local chemistry of the vein. The pumpellyites are plotted on an AFM diagram (Figure 4.5) with the compositional fields of pumpellyites from Vancouver Island, Upper Wakatipu,

FIGURE 4.4.1. FeO(t) vs  $Al_2O_3$  for pumpellyite from the Conwy Valley. Also shown are the compositional fields of pumpellyite from Vancouver Island (Surdam, 1969), Upper Wakatipu (Kawachi, 1975) and Loeche (Coombs et al., 1976).

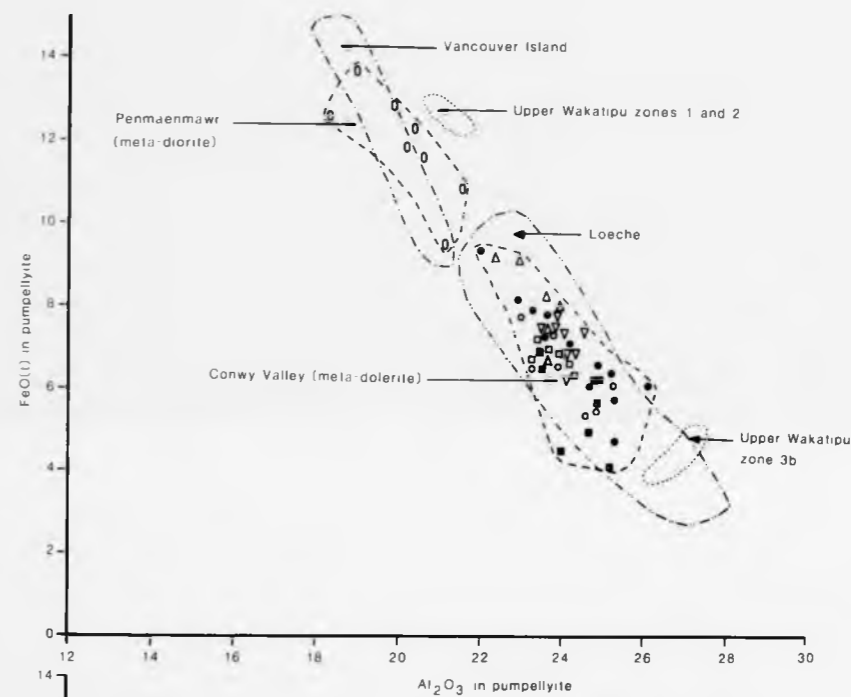


FIGURE 4.4.2. Mean FeO(t) vs  $Al_2O_3$  for pumpellyites from individual meta-dolerite samples from the Conwy Valley. The cross represents one standard deviation for FeO(t) and  $Al_2O_3$ .

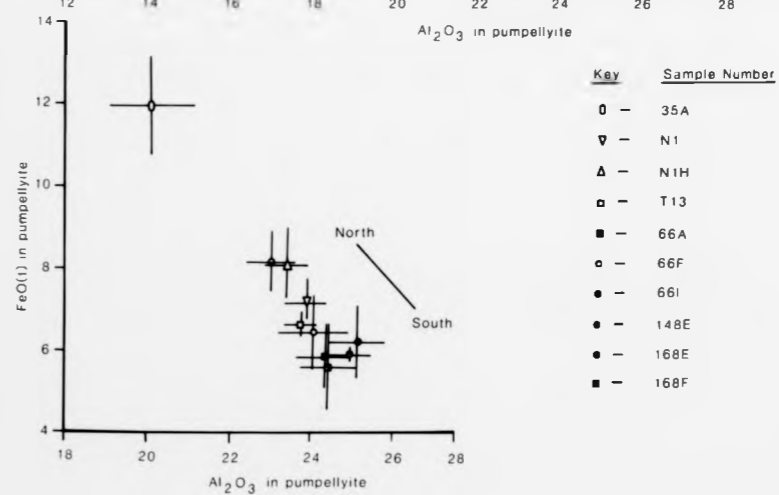
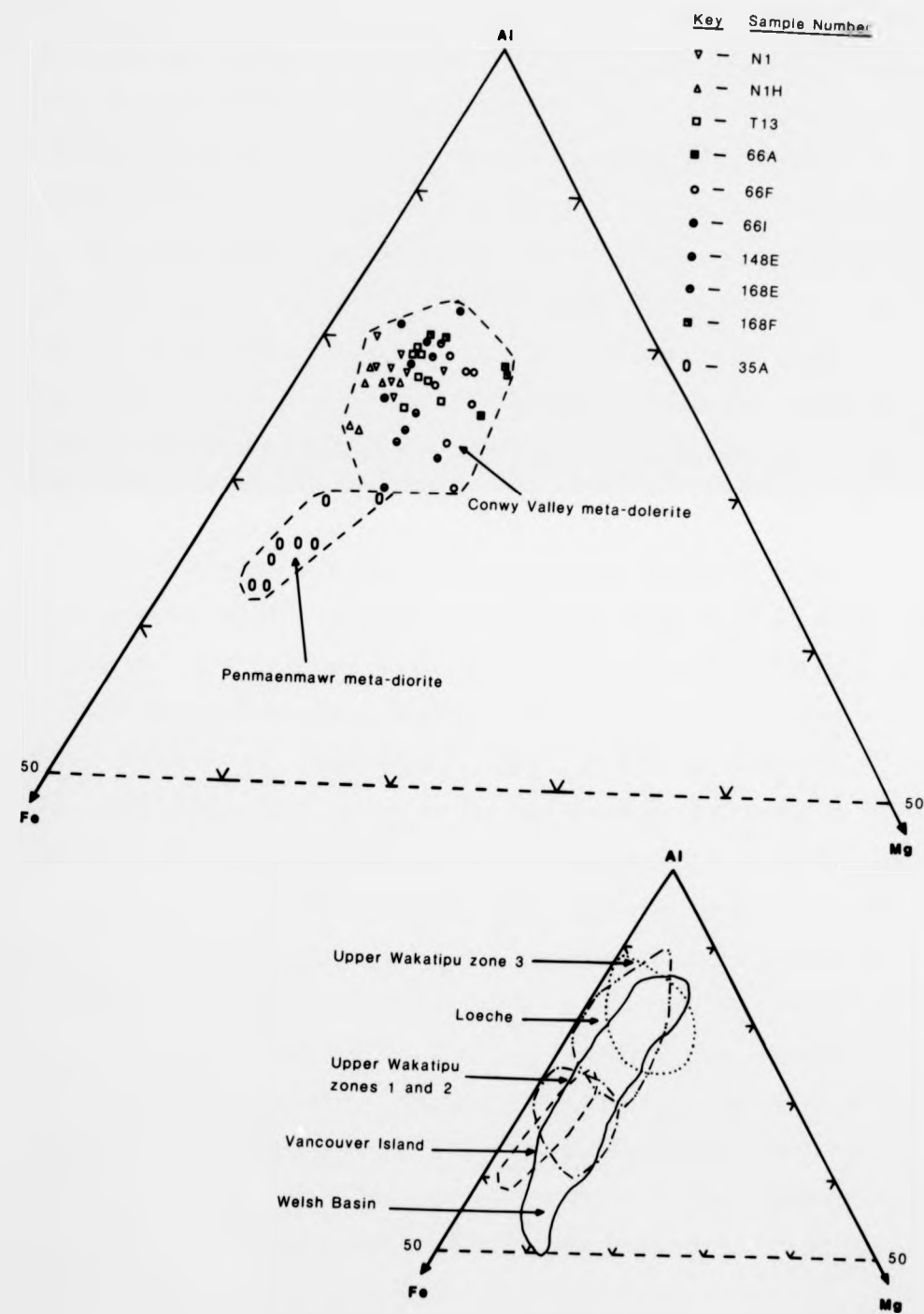


FIGURE 4.5. Al - Fe- Mg for pumpellyite from the Conwy Valley. Also shown are the compositional fields of pumpellyites from Vancouver Island (Surdam, 1969), Upper Wakatipu (Kawachi, 1975), Loeche (Coombs et al., 1976) and the Welsh basin (Bevins and Rowbotham, 1983).



Loeche and the Welsh basin (Bevins and Rowbotham, 1983) shown. Comparison of the compositional data for pumpellyites from the Conwy Valley with that of Bevins and Rowbotham (1983) from throughout the Welsh basin indicates that the Conwy Valley samples represent the relatively more aluminous pumpellyites of the Welsh basin. None of the particularly Fe-rich varieties typical of, for example, Builth Wells occur within the Conwy Valley. Pumpellyites from the Conwy Valley meta-dolerites plot close to those from Upper Wakatipu (Zone III) and Loeche which are thought to be typical of the pumpellyite-actinolite facies (Kawachi, 1975; Coombs et al., 1976). Pumpellyites from the Penmaenmawr intrusion plot close to those from Upper Wakatipu (Zones I and II) and Vancouver Island and are thought to be typical of the prehnite-pumpellyite facies (Surdam, 1969).

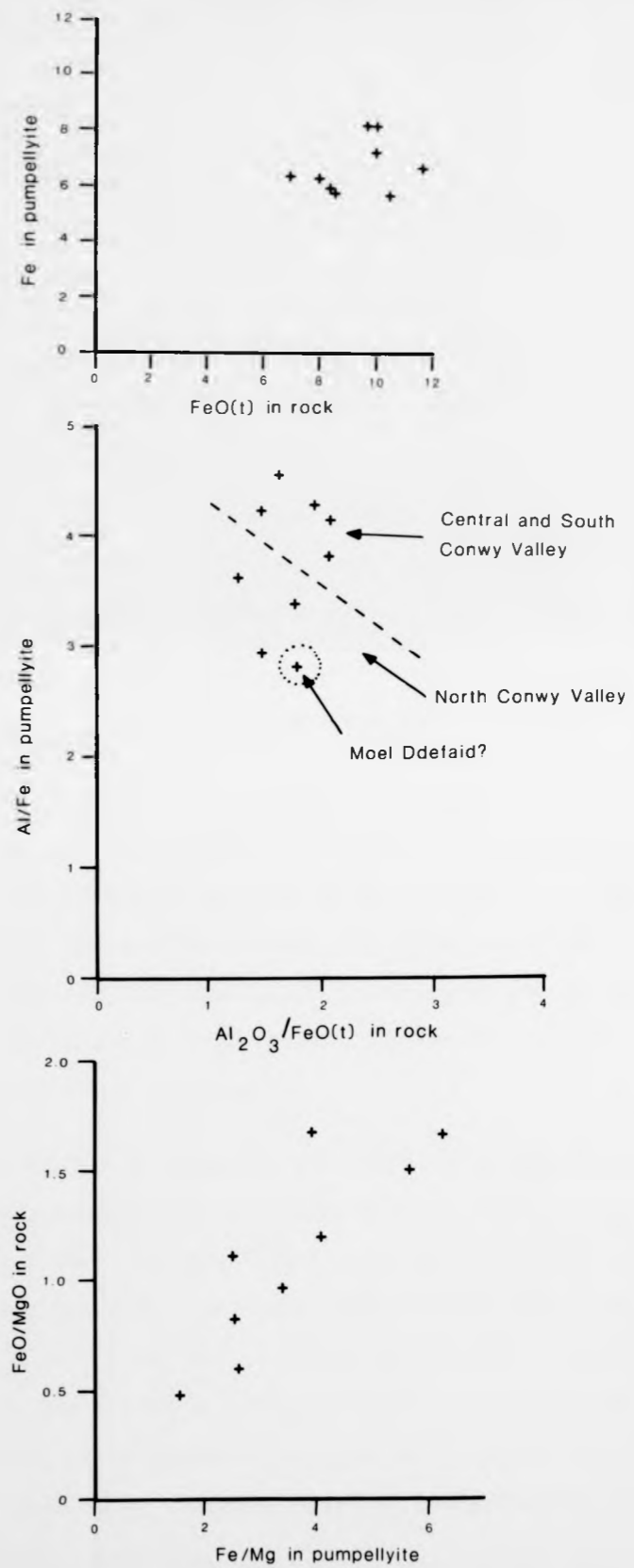
Several workers have observed a progressive increase in pumpellyite Al/Fe with increasing metamorphic grade (Bishop, 1972; Kawachi, 1975; Liou et al., 1983). Others have argued that host composition plays a critical role in the control of pumpellyite chemistry (Coombs et al., 1976; Offler et al., 1981; Nystrom, 1983). In order to assess the importance of bulk rock effects on the hand specimen scale Fe/Mg vs  $\text{FeO}^*/\text{MgO}$ , Al/Fe vs  $\text{Al}_2\text{O}_3/\text{FeO}^*$  and Fe vs  $\text{FeO}^*$  (where  $\text{FeO}^*$  = total iron as FeO) are plotted for pumpellyites and host rocks (Figures 4.6.3., 4.6.2. and 4.6.1. respectively). Clearly only the Fe/Mg ratio (Figure 4.6.3) displays any significant relationship between bulk rock chemistry and pumpellyite composition. It would appear, therefore, that relative location within the Conwy Valley, rather than host rock chemistry, is the major controlling influence on Al : Fe in pumpellyite. These observations might support the view that variation in pumpellyite chemistry is influenced by metamorphic parameters (pressure, temperature, fluid chemistry, etc) as well as host rock chemistry.



FIGURE 4.6.1. Pumpellyite Fe vs bulk rock FeO\* (total iron as FeO).

FIGURE 4.6.2. Pumpellyite Al/Fe vs bulk rock Al<sub>2</sub>O<sub>3</sub>/FeO\* (total iron as FeO).

FIGURE 4.6.3. Pumpellyite Fe/Mg vs bulk rock FeO\*/MgO (total iron as FeO).



#### 4.3.2. Prehnite.

Prehnite has been recognised in 56 samples of meta-dolerite from northern Snowdonia (Figure 4.3.2). Three characteristic forms of prehnite occur:-

- i) fans or patches of small crystals occurring in the groundmass, the interstitial alteration sites or occasionally in albitised feldspars.
- ii) minute flakes scattered throughout the groundmass or, more commonly, within albitised feldspars. Often these flakes are difficult to distinguish from white mica due to the small grain size and superficially similar optical characteristics.
- iii) relatively large (0.3mm) fans or subhedral crystals associated with pumpellyite and epidote in the Penmaenmawr intrusion.

Under the microscope the prehnites are invariably colourless and generally very clear and inclusion free. The larger fans and crystals display the incomplete and wavy extinction typical of the mineral (Deer et al., 1962). Maximum interference colours are second order and no anomalous purple or blue interference colours were observed (Surdam, 1969). In the minute prehnite flakes extinction is parallel and maximum birefringence is lower second order.

There have been 32 representative prehnite analyses made on 8 samples mainly from the northern Conwy Valley but the analyses do include two prehnite flakes from Moel Siabod (16 of these prehnite analyses are presented in Appendix 5). The basic formula of prehnite is  $\text{Ca}_2 (\text{Al,Fe}) (\text{Al Si}_3) \text{O}_{10} (\text{OH})_2$  (Liou et al., 1983). Substitution of  $\text{Ca}_2 \text{Fe}^{3+} \text{Al Si}_3 \text{O}_{10} (\text{OH})_2$  for  $\text{Ca}_2 \text{Al}_2 \text{Si}_3 \text{O}_{10} (\text{OH})_2$  is generally less than 10% but occasionally is up to 20% and very rarely can be as high as 40% (Surdam, 1969). The Conwy Valley prehnites show little compositional variation and are aluminous containing little or no  $\text{Fe}^{3+}$ . Prehnites from sample

FIGURE 4.7. Ca - Al- Fe diagram for prehnites from the Conwy Valley. Also shown is the compositional field of prehnite from Vancouver Island (Surdam, 1969) and a prehnite analysis from Upper Wakatipu (Kawachi, 1975).

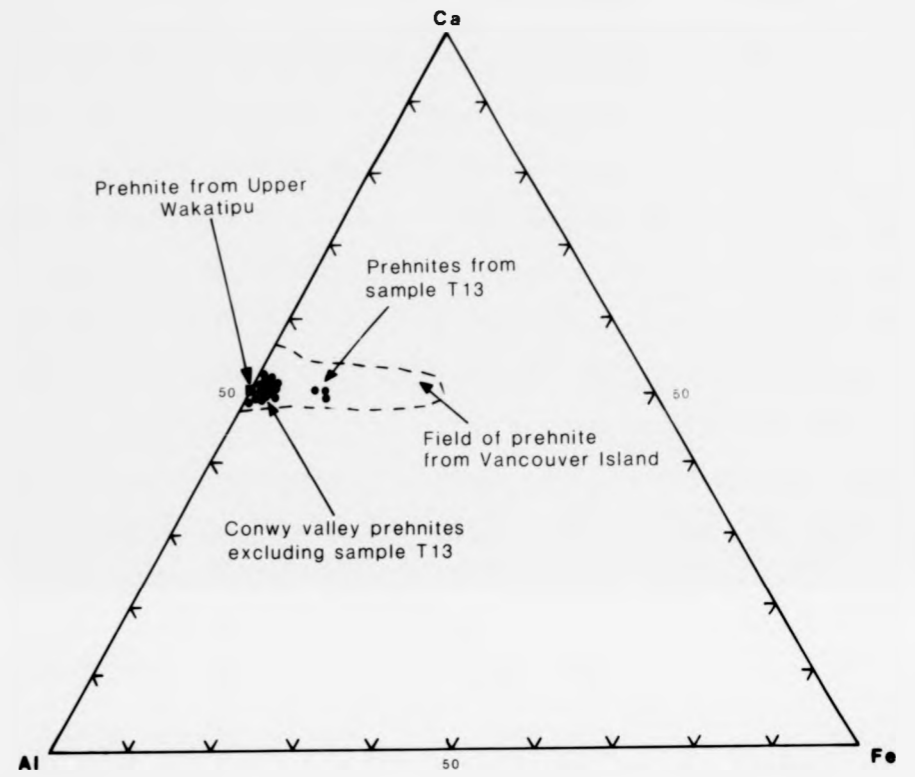
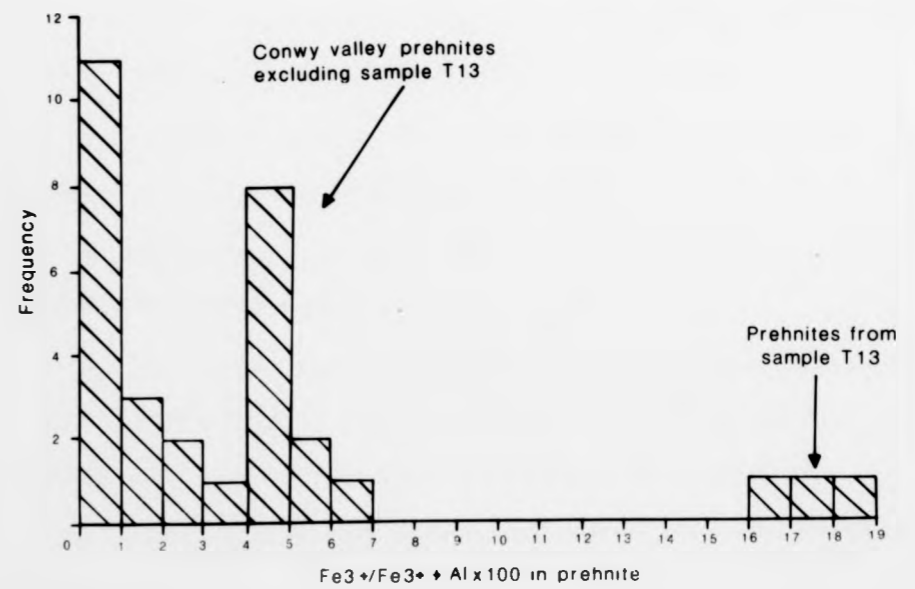


FIGURE 4.8. A histogram showing the  $Fe^{3+}/Fe^{3+} + Al \times 100$  contents of prehnites from the Conwy Valley.



T13 are exceptional and display about 19%  $\text{Fe}^{3+}$  substitution for Al. This is demonstrated on an ACF plot (Figure 4.7) and a histogram (Figure 4.8). Comparison of the prehnite compositional data of the Conwy Valley with that obtained by Bevins and Rowbotham (1983) from throughout Wales indicates that most Welsh prehnite contains little  $\text{Fe}^{3+}$ . Only prehnite from the peripheral parts of the Welsh basin contain significant  $\text{Fe}^{3+}$ , for example, Builth Wells (25% substitution of  $\text{Fe}^{3+}$  for Al) and Anglesey (17% substitution of  $\text{Fe}^{3+}$  for Al). Elsewhere substitution of  $\text{Fe}^{3+}$  for Al is < 10%. Liou et al. (1983) conclude that the  $\text{Fe}^{3+}/\text{Al}$  ratio of prehnite is dependent on pressure, temperature and  $f\text{O}_2$  with more aluminous prehnites indicating higher temperatures and/or less oxidising conditions.

#### 4.3.3. Epidote

Epidote minerals (clinozoisite and epidote) have been recognised in 159 of the meta-dolerites from northern Snowdonia (Figures 4.9.1., 4.9.2. and 4.9.3). Several characteristic forms of epidote occur:-

- i) idioblastic crystals associated, and in textural equilibrium, with chlorite  $\pm$  actinolite in the interstitial alteration sites.
- ii) small subhedral crystals or anhedral spongy masses within the groundmass, often the spongy epidotes are cloudy.
- iii) frequently cloudy, yellow or brown subhedral or anhedral epidotes within albitised feldspars.
- iv) large (> 0.3 mm) subhedral/euhedral crystals developed prevasively in epidote-rich meta-dolerites irrespective of alteration site and associated with albite + chlorite  $\pm$  actinolite  $\pm$  stilpnomelane.
- v) in veins associated with prehnite and pumpellyite in the Penmaenmawr intrusion.

FIGURE 4.9.1. Pistacitic, prismatic epidote in an epidote rich meta-dolerite, sample 85C (Cwm Eigiau). XP. X35.



FIGURE 4.9.2. Clinozoisitic epidote, displaying characteristic blue birefringence colours, associated with chlorite in an interstitial alteration site, sample 66L (Cerrig Cochion). XP. X35.



FIGURE 4.9.3. Continuously zoned epidotes from relatively Fe-rich core to Fe-poor rim, sample 168F (Moe1 Siabod). XP. X85.



FIGURE 4.9.1. Pistacitic, prismatic epidote in an epidote rich meta-dolerite, sample 85C (Cwm Eigiau). XP. X35.



FIGURE 4.9.2. Clinozoisitic epidote, displaying characteristic blue birefringence colours, associated with chlorite in an interstitial alteration site, sample 66L (Cerrig Cochion). XP. X35.



FIGURE 4.9.3. Continuously zoned epidotes from relatively Fe-rich core to Fe-poor rim, sample 168F (Moel Siabod). XP. X85.

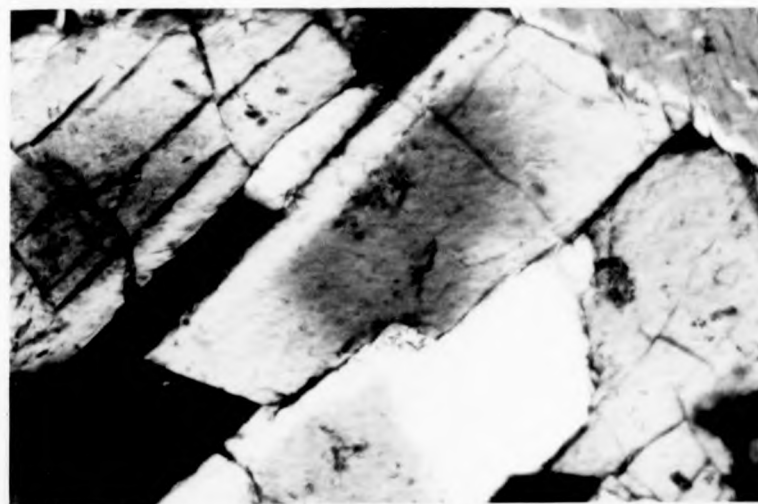


FIGURE 4.9.2. Pleistochroic, anhedral epidote in an epidote-rich metachertite, sample 65C (Cwm Eglwys), XP, X35.

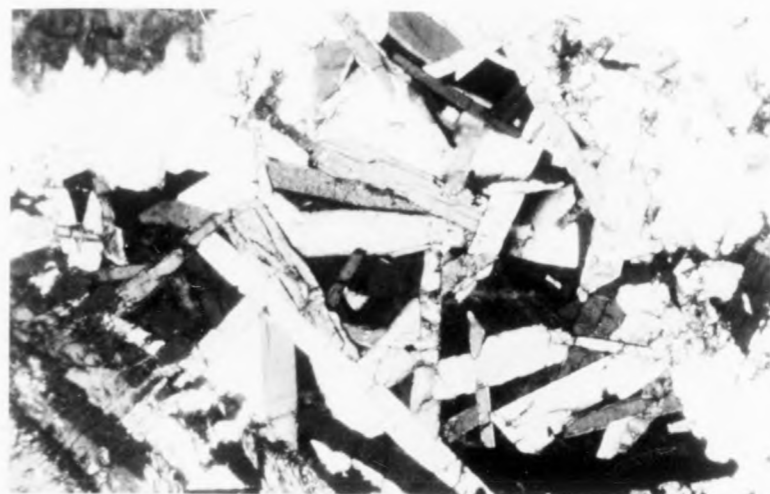


FIGURE 4.9.3. Pleistochroic epidote, displaying characteristic blue birefringence colors, associated with polarization in an interstitial alteration site, sample 66L (Cwm Eglwys), XP, X35.

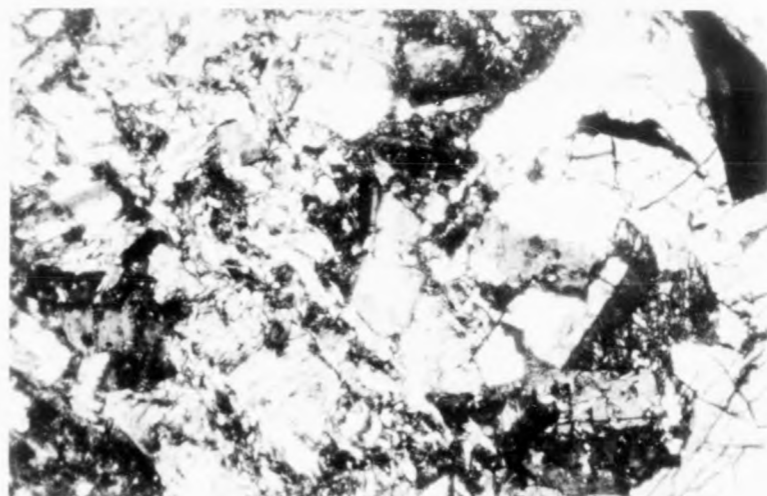
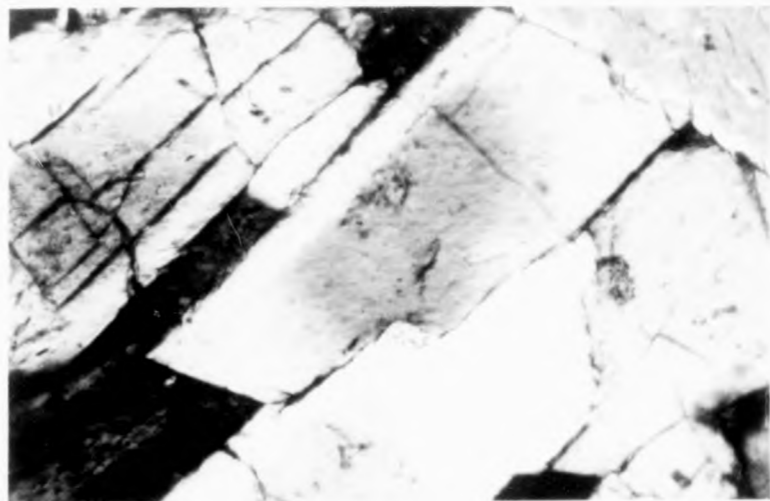


FIGURE 4.9.3. Continuously zoned epidotes from relatively Fe-rich core to Fe-poor rim, sample 168F (Moel Siabod), XP, X85.

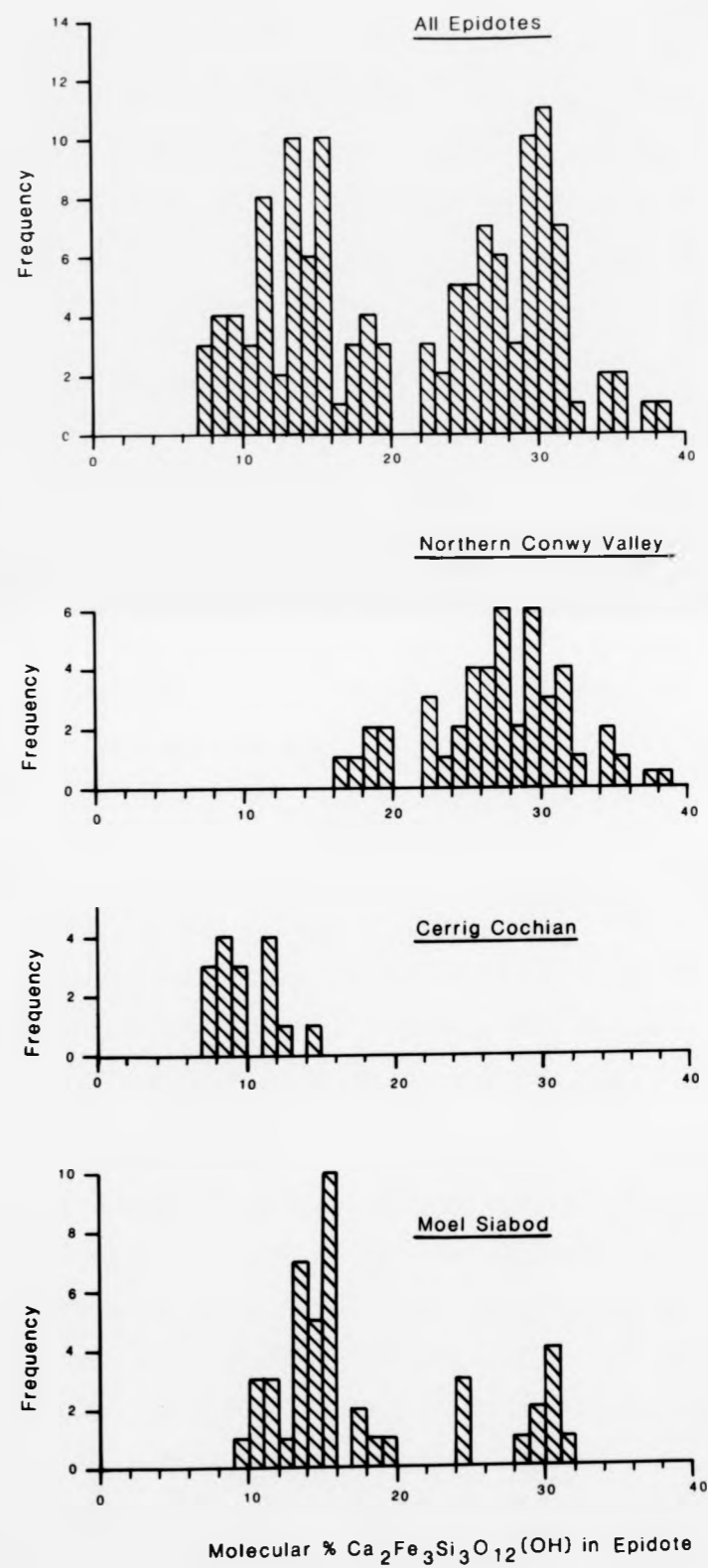


Optically the epidotes are quite variable, ranging from a markedly pleochroic ( $\alpha$  = colourless,  $\beta$  = light yellow,  $\gamma$  = yellow) through a slightly pleochroic ( $\alpha$  = colourless,  $\beta$  = colourless,  $\gamma$  = light yellow) to a colourless variety. Epidote colour reflects the replacement of Al by  $\text{Fe}^{3+}$  (Deer et al., 1962) where the depth of colour reflects a greater substitution of  $\text{Fe}^{3+}$  for Al. Frequently zoning is present with the cores being more strongly coloured (Fe-rich) than the rims. In addition they are often cloudy and are then brown or grey in colour, which could indicate alteration of these epidotes. It would appear that Fe-rich epidotes are more prone to alteration with the cores of zoned crystals cloudy and the rims clear. Chemical zoning can be detected by the change of interference colours and slight differences in extinction angle. Optically there is no sharp break between Fe-rich cores and Fe-poor rims indicating that most of the zoning is continuous.

There have been 128 epidote analyses obtained including several traverses across individual zoned crystals (40 of the epidote analyses are presented in Appendix 5). Epidote formula recalculations have been made on a basis of 12.5 oxygens (Coombs et al., 1976) in a structural formula of  $X_2 Y_3 Z_3 (O, OH, F)_3$ ; where  $X = \text{Ca}$  and  $\text{Fe}^{2+}$ ,  $Y = \text{Al}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}$  and  $\text{Ti}$ , and  $Z = \text{Si}$  (Deer et al., 1962). There is significant variation in Al and Fe contents with a good negative correlation ( $r = -.97$ ) between the two suggesting substitution of one for the other. The relationship between optical properties and epidote chemistry in the Conwy Valley was readily confirmed with the transition between optical "clinzoisitic" and "pistacitic" epidotes occurring at about  $\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Al} \times 100 = 18 - 20$ . The most frequently observed maximum pistacitic (Ps) content ( $\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Al} \times 100$ ) is about 33%. In the literature there have been analyses recorded with up to 40% Ps content (Liou et al., 1983). The range of Ps substitution has been calculated for the Conwy Valley



FIGURE 4.10. Histograms showing the  $\text{Ca}_2\text{Fe}_3\text{Si}_3\text{O}_{12}(\text{OH})$  content (Ps) of epidotes from: i) throughout the Conwy Valley, ii) the northern Conwy Valley, iii) the Cerrig Cochion intrusion, and, iv) the Moel Siabod intrusion.



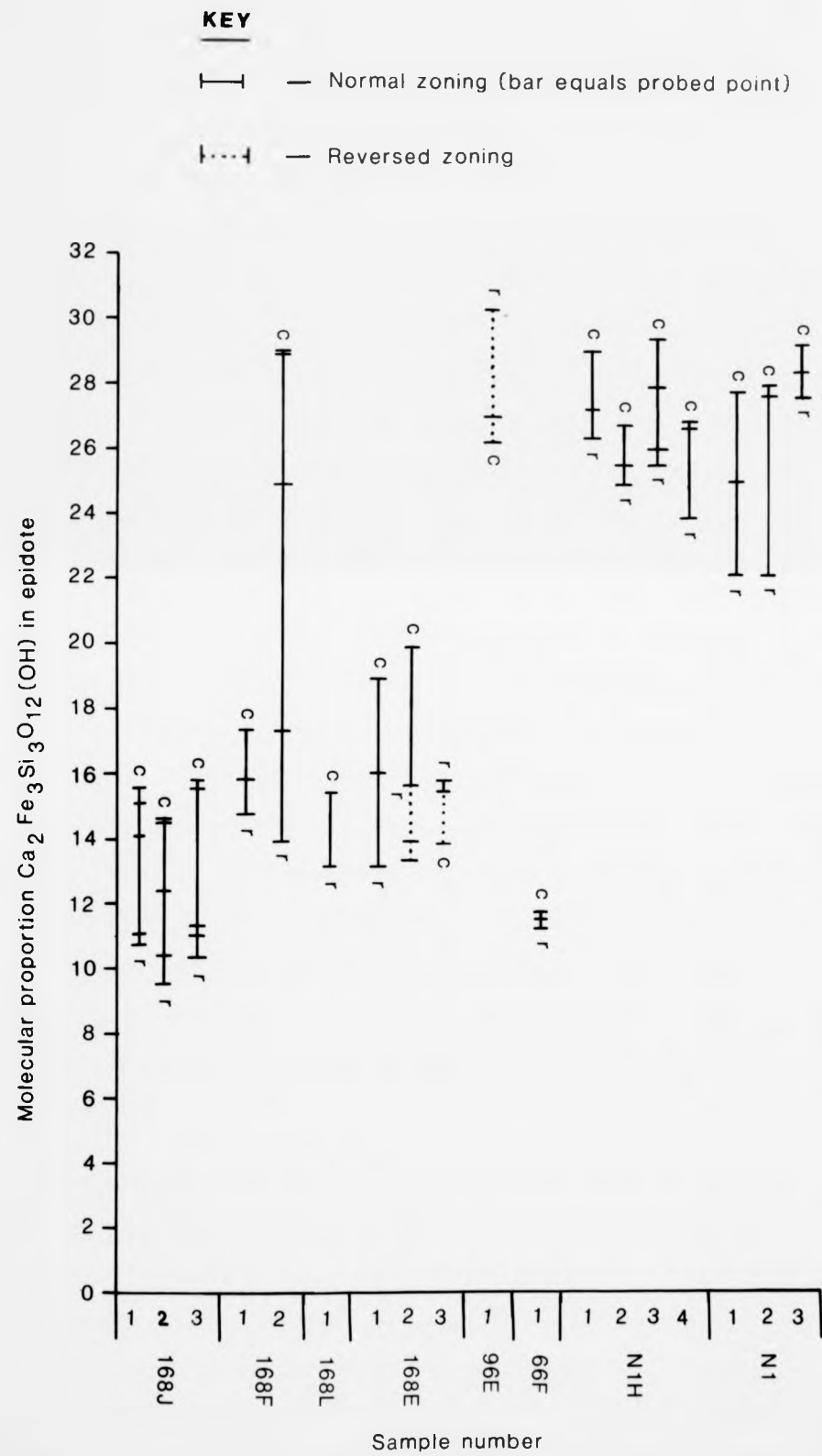
epidotes (Figure 4.10) and clearly there is a large range in Ps content (7-39%) with two maxima, one around  $Ps_{13-16}$  and a second around  $Ps_{29-31}$ . The Ps contents of epidotes from the intrusions of the northern Conwy Valley, Cerrig Cochion and Moel Siabod are also shown separately (Figure 4.10). In support of the optical observations significant and systematic variation in Ps content is seen within the Conwy Valley.

In several samples marked chemical zoning occurs (Figure 4.11). In all but one example the zoning is from relatively Fe-rich core to Fe-poor rim and is continuous in nature. When probing zoned crystals there may be difficulty in obtaining a true core composition as the thin section may cut the crystal some distance from the true core and thus yield only apparent core compositions. This problem is largely overcome by careful choice of crystal and traversing several zoned crystals in a sample. The change in chemistry from core to rim is usually 2 - 5% Ps but in one sample from Moel Siabod (168F) it is much greater (15% Ps).

Two samples (148E and 168E) contain epidotes which have markedly different compositions in different alteration sites. Both samples contain cloudy, brown, Fe-rich epidote ( $Ps > 25\%$ ) in the plagioclase sites and clear, idiomorphic, Fe-poor epidote ( $Ps < 20\%$ ) in the interstitial sites. This relationship was observed frequently in the meta-dolerites of northern Snowdonia.

Numerous experimental studies and field observations have indicated that there is correlation between epidote Ps and metamorphic parameters such as temperatures,  $fO_2$  and fluid composition (Miyashiro and Seki, 1958; Sigvaldason, 1962; Holdaway, 1972; Liou, 1973; Bird and Helgeson, 1981; Liou et al., 1983) with lower temperature crystallisation of Fe-rich epidote and higher temperature crystallisation of Fe-poor epidote. Host rock chemistry also appears to be an important influence on epidote

FIGURE 4.11. Chemical zoning in the epidotes from the Conwy Valley.



chemistry with Fe-rich hosts tending to develop more pistacitic epidotes at constant pressure, temperature and  $fO_2$  (Holdaway, 1972; Liou et al., 1983). Figures 4.12.1 and 4.12.2. show epidote PS content plotted against host rock  $Fe_2O_3^*/Fe_2O_3^* + Al \times 100$  (where  $Fe_2O_3^*$  = total iron as  $Fe_2O_3$ ) and  $FeO^*/MgO$  (where  $FeO^*$  = total iron as  $FeO$ ) respectively. Clearly it is possible to conclude from the observations that epidote composition is significantly influenced by host rock chemistry with higher host rock  $Fe_2O_3^*/Fe_2O_3^* + Al_2O_3$  and  $FeO^*/MgO$  ratios leading to the development of more PS-rich epidote. Thus it appears that both metamorphic parameters and host rock composition may influence epidote chemistry.

Potentially of greater use than bulk epidote compositions are the specific compositions of individual zoned epidotes as changes in chemistry could reflect variation in metamorphic conditions. Coombs et al. (1976) argue that with increasing metamorphic grade  $fO_2$  will progressively fall resulting in the crystallisation of an increasingly aluminous epidote with early Fe-rich epidote overgrown by later Fe-poor epidote. Kawachi (1975) supported this conclusion in Upper Wakatipu by the observation of Fe-rich epidote in the prehnite-pumpellyite facies areas which is only overgrown by Fe-poor epidotes in the pumpellyite - actinolite facies areas. Bishop (1972) also describes a similar sequence of events where Fe-rich epidote is overgrown by a later, higher grade Fe-poor epidote.

It is possible, therefore, that the epidote zoning in the Conwy Valley could indicate continuous crystallisation over a period of time during which temperatures increased and  $fO_2$  decreased. The presence of exceptionally Fe-rich epidotes ( $Ps_{32-39}$ ) in sample T13 is consistent with the presence of Fe-rich prehnite, both of which could indicate locally enhanced  $fO_2$ .

FIGURE 4.12.1. Epidote Ps content vs bulk rock  $\frac{\text{Fe}_2\text{O}_3^*}{\text{Fe}_2\text{O}_3^* + \text{Al}_2\text{O}_3} + \text{Al}_2\text{O}_3$  X 100 (total iron as  $\text{Fe}_2\text{O}_3$ ).

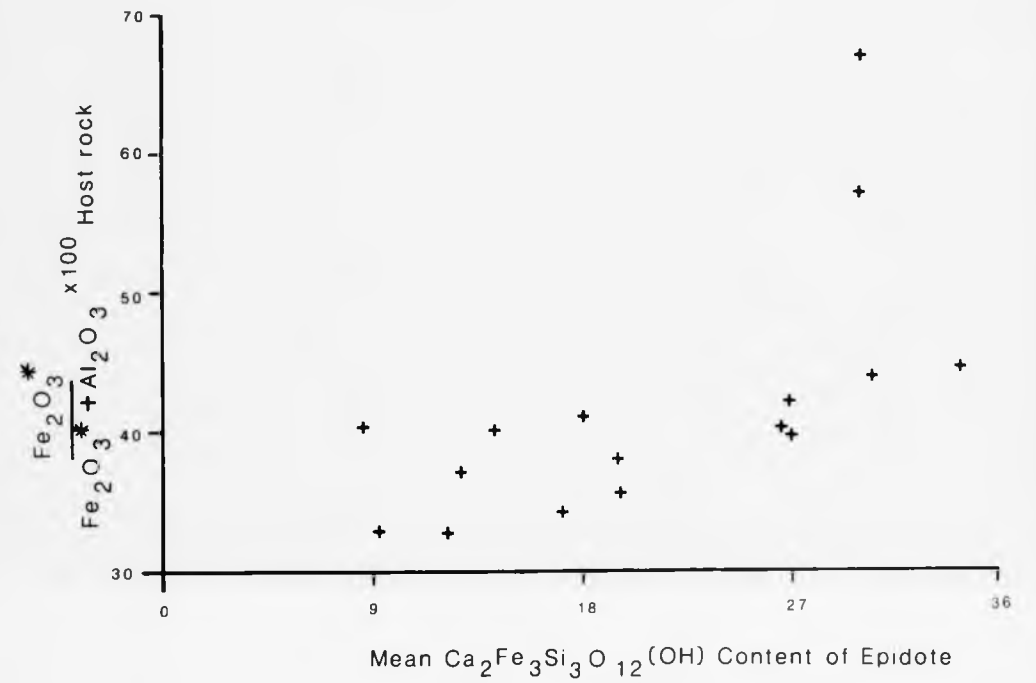
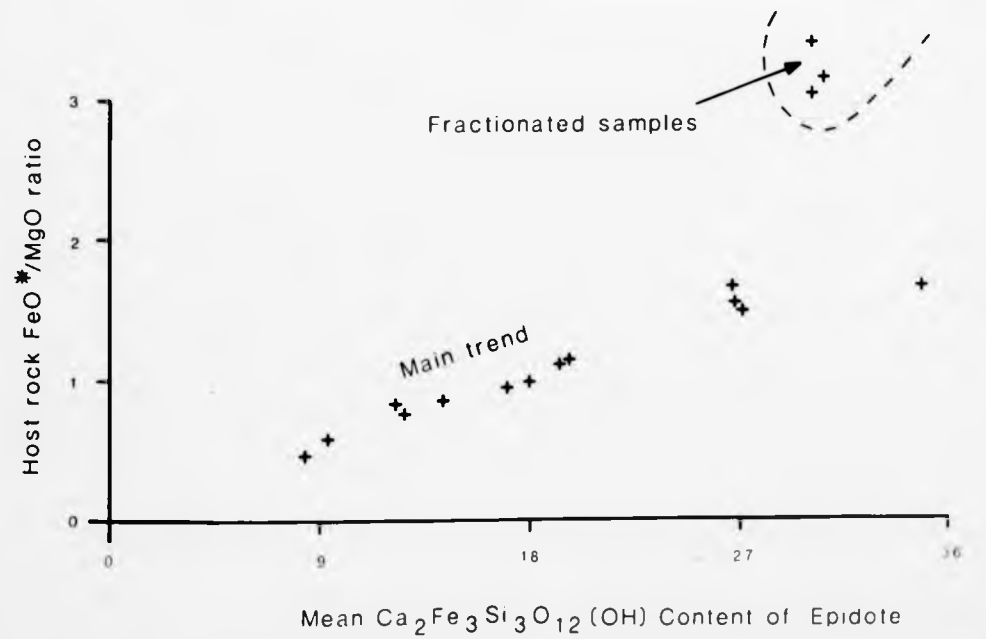


FIGURE 4.12.2. Epidote Ps content vs bulk rock FeO\*/MgO ratio (total iron as FeO).



#### 4.3.4. Chlorite

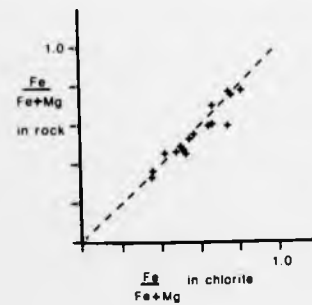
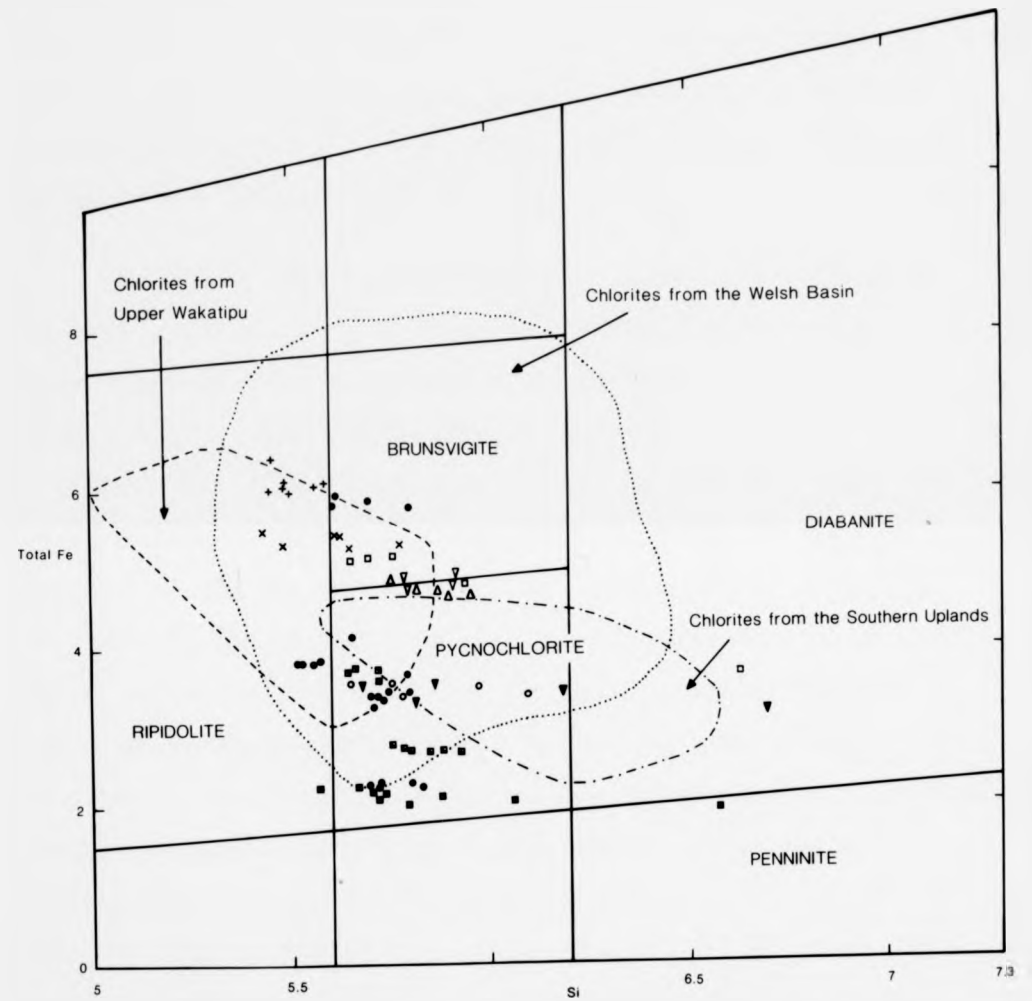
Chlorite is the most common secondary mineral developed in the meta-dolerites of northern Snowdonia and several characteristic forms occur including:-

- i) sub-rounded to angular masses of plates and flakes within the interstitial alteration sites and often associated with idioblastic epidote and acicular amphibole and occasionally with pumpellyite or stilpnomelane.
- ii) anhedral small patches within the groundmass.
- iii) small patches or veins within albitised feldspars.
- iv) rounded or sub-rounded pseudomorphs possibly after olivine which occur in several of the least differentiated samples, particularly from Cerrig Cochion and Tal-y-Fan.
- v) partial replacement of clinopyroxene, sometimes in association with actinolite.

Optically the chlorites display little variation. Almost all are a light or very light green colour. Intensity of colour in chlorites appears to be related to chemistry with stronger colours reflecting higher Fe contents (Deer et al., 1962). Birefringence colours are typically low and are often anomalous in striking blues and browns. Under crossed polars the chlorites are often very dark. Some of the larger chlorite-rich areas are composed of sheaves and tiny plates and, occasionally, different areas within a mass contain sheaves of chlorite with different, anomalous, brown and blue interference colours.

There have been 82 chlorite analyses obtained from the Conwy Valley meta-dolerites (16 of these are presented in Appendix 5). Chlorite recalculation is on a basis of 14 oxygens in a structural formula of

FIGURE 4.13. Si vs total Fe diagram of Hey (1954). Showing the composition of the Conwy Valley chlorites. Also shown are the compositional fields of chlorites from Upper Wakatipu (Kawachi, 1975), the Southern Uplands (Oliver and Leggett, 1980) and the Welsh basin (Bevins and Rowbotham, 1983). Also shown is Fe/Fe+Mg in host rock vs Fe/Fe+Mg in chlorite.



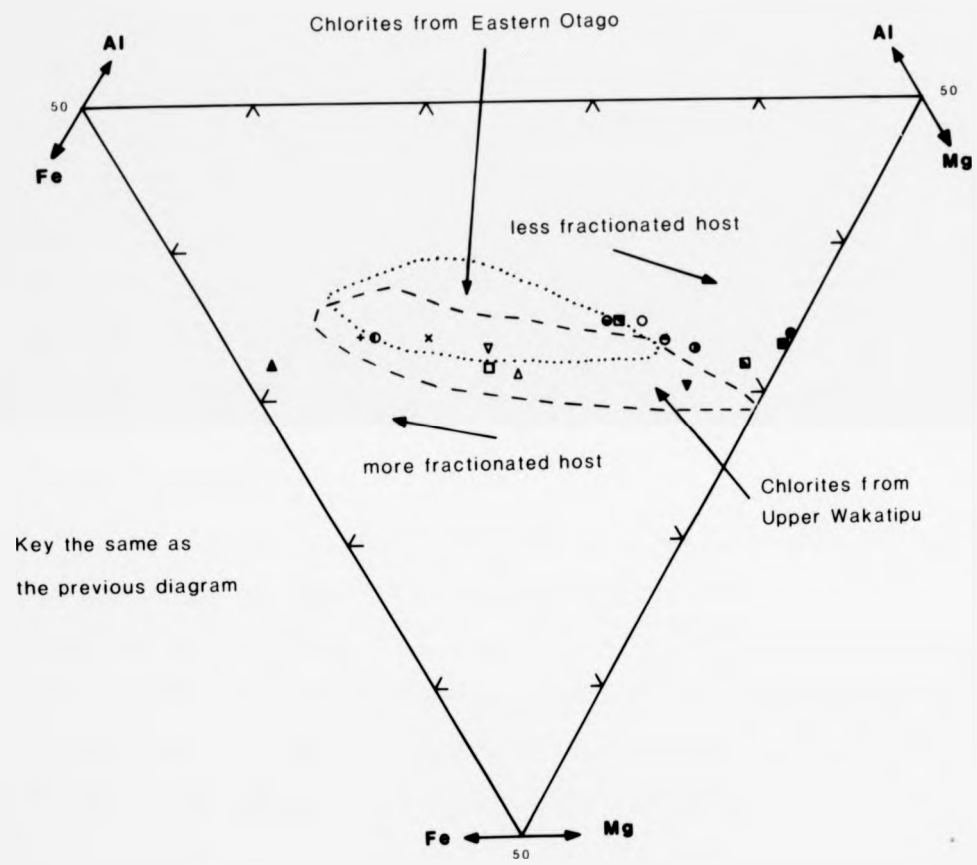
Key	Sample Number	Sample Number
▽	N1	+ - 85A
△	N1H	x - 96E
▲	N1K	● - 148E
▼	T6	○ - 168E
□	T13	■ - 168F
■	66A	■ - 168J
○	66F	● - 168L
●	66I	● - 169R3

$Y_6 Z_4 O_{10} (OH)_8$ ; where  $Y = Si$  and  $Al$  and  $Z = Al, Fe^{3+}, Fe^{2+}, Mn, Mg$  and  $Ca$ . This recalculation assumes that the tetrahedral sites are filled with  $Si$  and  $Al$  and any residual  $Al$  enters the octahedral sites. Most analyses display little variation in  $Si$  and  $Al$  contents in contrast to a marked variation in  $Fe$  and  $Mg$  contents. Only trace concentrations of  $Mn$  and  $Ca$  were detected in many analyses.

The chlorite results are plotted on the  $Si$  vs total  $Fe$  diagram of Hey (1954) (Figure 4.13). Although the analyses show great variation, those from individual samples tend to display little variation, an observation also made in other areas of low-grade metamorphism (Kawachi, 1975; Coombs et al., 1976; Bevins and Rowbotham, 1983). The most common chlorite analyses are pycnochlorite (55%) with fewer ripidolites (21%) and brunsvigites (21%). Also shown, for comparison, are the compositional fields for chlorites from Upper Wakatipu (Kawachi, 1975), the Southern Uplands (Oliver and Leggett, 1980) and the Welsh basin (Bevins and Rowbotham, 1983). The first two areas display a more restricted compositional range than the Conwy Valley chlorites. Chlorites from throughout the Welsh basin, however, display a significantly broader compositional range than those from the Conwy Valley. Chlorites from both Llyn and Pembrokeshire contain more  $Fe$  than most of the Conwy Valley chlorites thus accounting for the extended compositional field. The mean chlorite data are plotted on an AFM diagram (Figure 4.14) which demonstrates the relatively constant  $Al$  and variable  $Fe$  and  $Mg$  contents of the chlorites. Compositional fields of chlorites from Upper Wakatipu (Kawachi, 1975) and Otago (Brown, 1967) are also shown and closely correspond to those of the Conwy Valley. Chlorites crystallised in the zeolite facies (Boles and Coombs, 1977) generally contain significantly more  $Si$  (> 6  $Si$  ions in the formula) than those crystallised at higher grades (< 6  $Si$  ions in the formula), such as those from the Conwy Valley.



FIGURE 4.14. Al - Fe - Mg for chlorites from the Conwy Valley. Also shown are the compositional fields of chlorites from Otago (Brown, 1967) and Upper Wakatipu (Kawachi, 1975).



Kawachi (1975) examined variation in Fe and Mg in chlorites and concluded that the major control on chlorite chemistry is the host rock composition where high FeO/FeO + MgO in the host rock leads to high  $\Sigma\text{Fe}/(\Sigma\text{Fe} + \text{Mg})$  in chlorites. Positive correlation coefficients of .85, .89 and .84 were calculated for bulk rock FeO/MgO, FeO\*/MgO (where FeO\* = total iron as FeO) and Fe<sub>2</sub>O<sub>3</sub>/MgO plotted against chlorite  $\Sigma\text{Fe}/\Sigma\text{Fe} + \text{Mg}$  respectively. Also shown in Figure 4.13 is a plot of chlorite Fe/Fe + Mg against bulk rock Fe/Fe + Mg and the influence of host chemistry on mineral composition is evident. As a result, any systematic trend in chlorite Fe/Mg as grade changes is likely to be masked by the effects of host rock compositional control.

#### 4.3.5. Stilpnomelane

Stilpnomelane has been identified in 23 of the meta-dolerites from northern Snowdonia (Figure 4.15). It occurs as needles or radiating sheaves, often displaying a bow-like form, and is frequently associated with chlorite + albite ± actinolite ± epidote. Stilpnomelane typically occurs in the more fractionated meta-dolerites (Chapter 3) and as such is found most frequently in the albite rich meta-dolerites.

Optically stilpnomelane is very distinctive with a very intense brown, or, occasionally, green colour and strong pleochroism from  $\alpha$  = yellow,  $\beta$  = dark brown and  $\gamma$  = dark brown, or  $\alpha$  = yellow,  $\beta$  = green and  $\gamma$  = green. The differences in colour reflect variation in the oxidation state of iron with green being indicative of ferrostilpnomelane and brown indicative of ferristilpnomelane (Deer et al., 1962). Only one sample contains ferrostilpnomelane (Sample NIC) the rest ferristilpnomelane. The maximum interference colours are second order but are partially or totally masked by the strong colour of the mineral.

There have been 12 stilpnomelane analyses obtained (Figure 4.16)

FIGURE 4.15. (i) (upper) Ferristilpnomelane with chlorite (medium green), actinolite (light green), epidote (light yellow) and quartz, sample 179C (Moel Siabod). PPL. X14.  
(ii) (lower) Ferristilpnomelane with quartz and minor chlorite, sample 179C (Moel Siabod). PPL. X35.

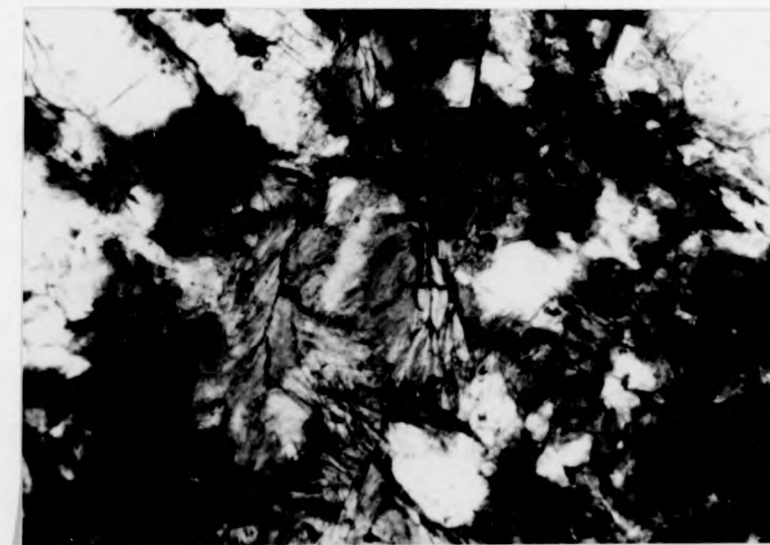
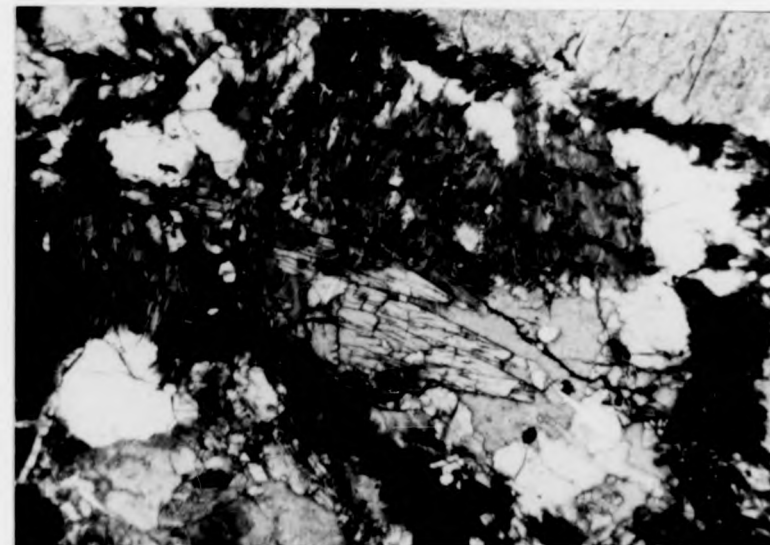
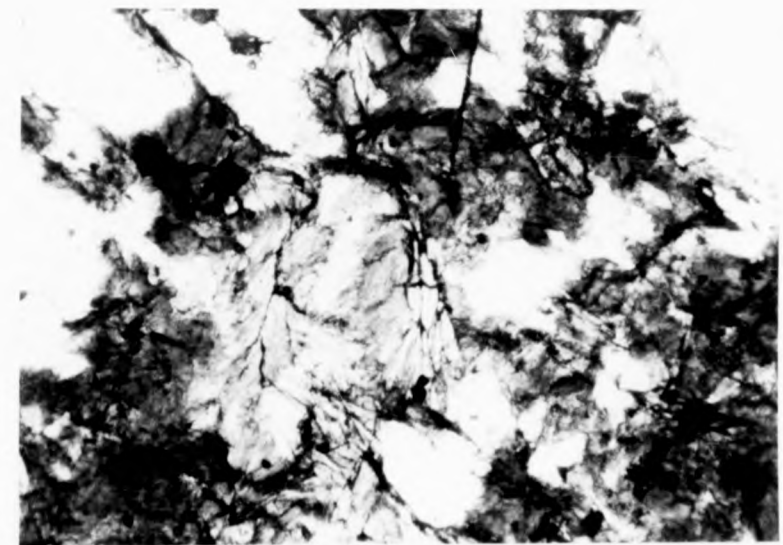
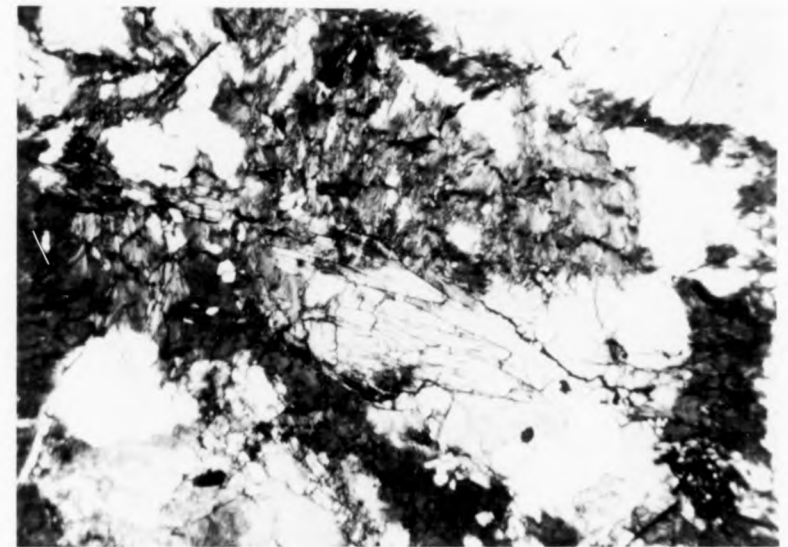
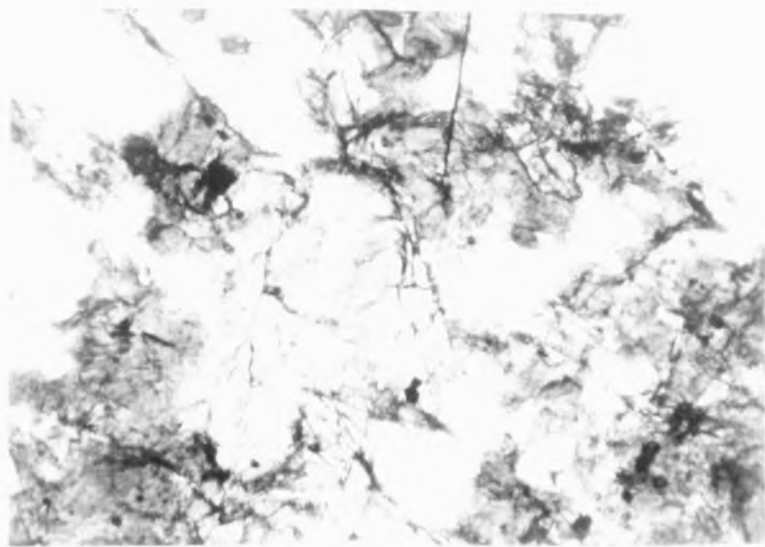
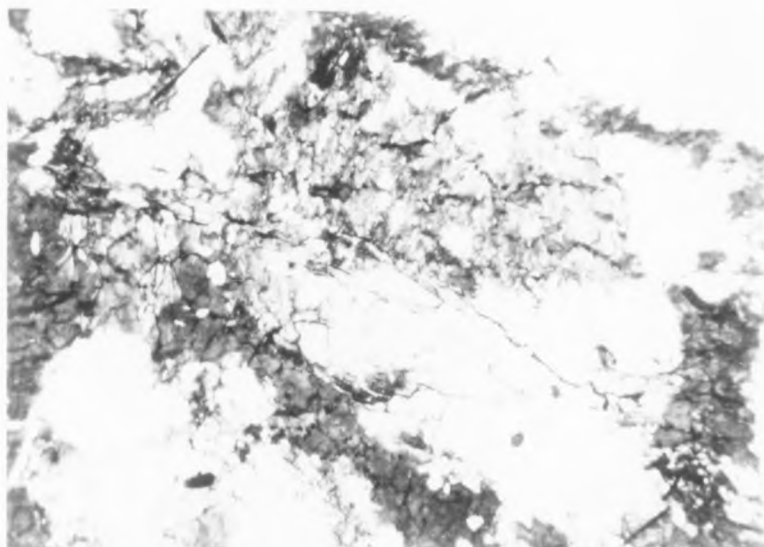


FIGURE 4.15. (i) (upper) Ferristilpnomelane with chlorite (medium green), actinolite (light green), epidote (light yellow) and quartz, sample 179C (Moel Siabod). PPL. X14.  
(ii) (lower) Ferristilpnomelane with quartz and minor chlorite, sample 179C (Moel Siabod). PPL. X35.





from two samples of meta-dolerite (2 analyses are presented in Appendix 5). The mineral recalculation has been made on the basis of 8 Si cations in the unit cell. Also shown are the stilpnomelane compositional fields from Upper Wakatipu (Kawachi, 1975), the Welsh basin (Bevins and Rowbotham, 1983) and northern Greenland (Bevins and Rowbotham, in press). Also shown are 4 ferrostilpnomelane analyses from Tal-y-Fan (Rowbotham, unpublished data). The Al contents of stilpnomelanes from all the areas are relatively constant with the main compositional variations being in Fe and Mg. This is thought, by Kawachi (1975), to reflect differences in host rock chemistry with stilpnomelanes from sediments containing more Fe than those from basic rocks.

#### 4.3.6. Sphene

Sphene is ubiquitous in the meta-dolerites of northern Snowdonia although it is often present only in small amounts. Two characteristic forms of sphene occur:-

- i) very small rounded aggregates of high relief scattered throughout the chlorite-rich groundmass and within the chlorite of the interstitial alteration sites. Occasionally sphene granules form nuclei around which later acicular amphiboles grow.
- ii) granular replacement of the ilmenite fraction of Fe - Ti oxides (Section 3.2.).

Optically sphene is readily identified by its very high relief and extreme birefringence, although most sphene aggregates are too small for detailed optical examination.

There have been 9 sphene analyses obtained (Figure 4.17) from 4 of the meta-dolerites of the Conwy Valley (4 analyses are presented in Appendix 5). Mineral recalculations have been made on the basis of 4

FIGURE 4.16. Al - Fe - Mg for stilpnomelanes from the Conwy Valley. Also shown are the compositional fields of stilpnomelanes from Upper Wakatipu (Kawachi, 1975), the Welsh basin (Bevins and Rowbotham, 1983) and Greenland (Bevins and Rowbotham, in press).

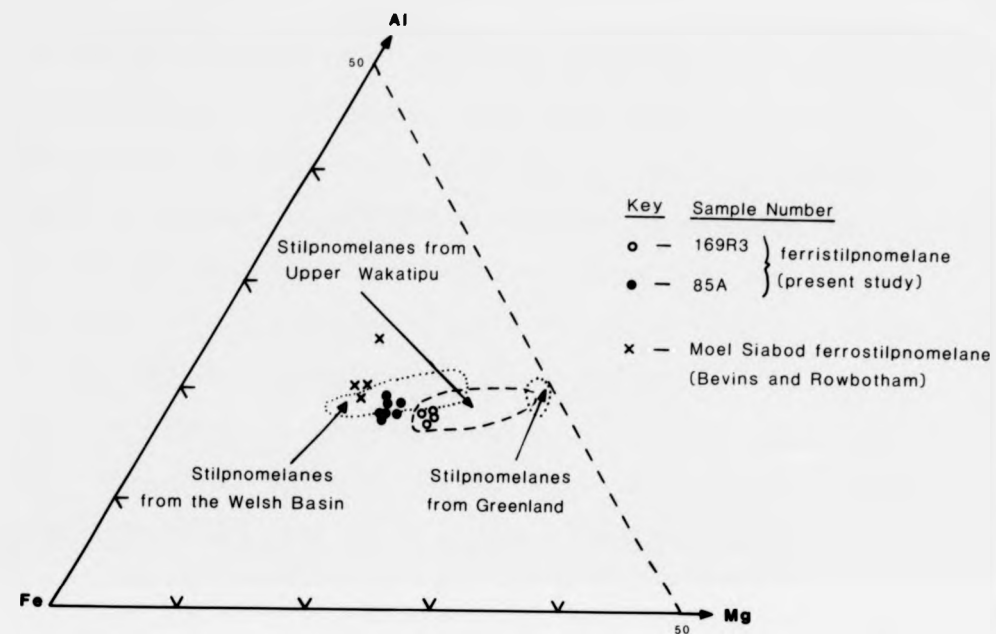
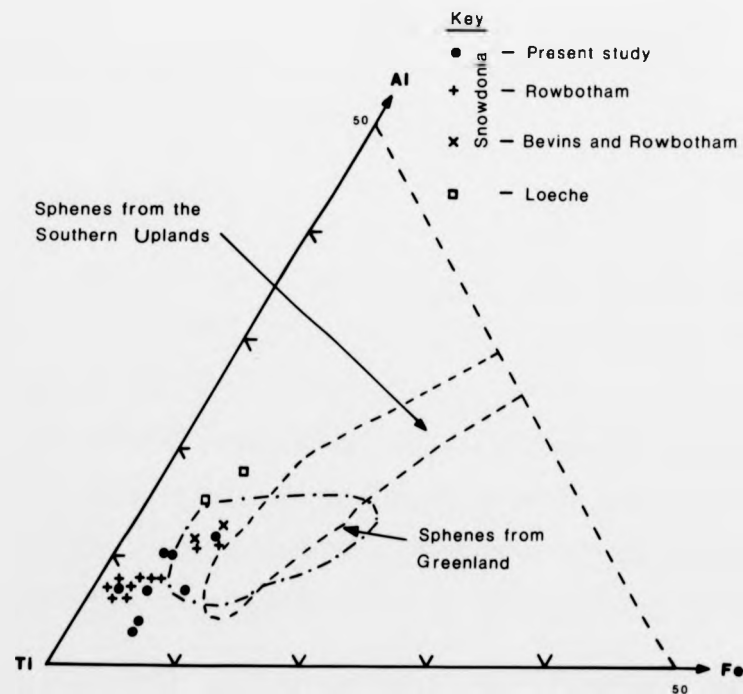


FIGURE 4.17. Al - Ti - Fe for sphenes from the Conwy Valley. Also shown are the compositional fields of sphenes from the Southern Uplands (Oliver and Leggett, 1980) and Greenland (Bevins and Rowbotham, in press).



Si cations per unit cell (Coombs et al., 1976). In addition to the sphenes of the present study unpublished sphenes from the Conwy Valley by Rowbotham (11 analyses from Cerrig Cochion and Moel Siabod) and two published analyses from Haffodty Farm (Bevins and Rowbotham, 1983) are included. It can be seen that there is marked variation in sphenes composition with significant substitution of Al and  $\text{Fe}^{3+}$  for Ti. For comparison the compositional fields of sphenes from Loeche (Coombs et al., 1976) the Southern Uplands (Oliver and Leggett, 1980) and northern Greenland (Bevins and Rowbotham, in press) are also shown. The sphenes from the Conwy Valley contain more Al and less  $\text{Fe}^{3+}$  than those from Scotland and less Fe + Al than those from Loeche.

In general, sphenes compositions are rather variable and sphenes of similar composition can be produced in different environments (Coombs et al., 1976). However, Boles and Coombs (1977) consider that the substitution of Al and  $\text{Fe}^{3+}$  for Ti is typical of low-grade metamorphic sphenes.

#### 4.3.7. Amphibole

Amphibole has been recognised in 165 of the meta-dolerites from northern Snowdonia (Figures 4.18.1 and 4.18.2). Two characteristic forms of amphibole occur:-

- i) epitaxial overgrowths around relict igneous clinopyroxenes.
- ii) isolated acicular needles, or groups of needles, which are most abundant in the interstitial alteration sites associated with, and occasionally overgrowing, chlorite and idioblastic epidote.

Epitaxial amphibole around clinopyroxene occurs throughout northern Snowdonia. Acicular amphibole also occurs throughout northern Snowdonia but is most pervasively developed in central northern Snowdonia and the central Conwy Valley. Hashimoto (1972) describes both forms of amphibole



and argues that only the acicular amphibole reflects the metamorphic conditions, the epitaxial amphibole being influenced more by kinetics than pressure and temperature. As a result of this possible problem, only the clearly metamorphic needles of actinolite were included in the petrographic descriptions of secondary mineral assemblages (Chapter 3).

Optically the amphibole is distinctive with a characteristic acicular or epitaxial form. Usually the amphibole is colourless or very light green in colour and when coloured it has the following pleochroic scheme:  $\alpha$  = colourless,  $\beta$  = colourless and  $\gamma$  = light green. Occasionally darker green actinolites occur associated with stilpnomelane and pistacitic epidote in the more fractionated meta-dolerites. Colour in the tremolite-actinolite series reflects iron content where the stronger the colour the higher the Fe content (Deer et al., 1962). Maximum interference colours are a distinctive middle second order blue/green. Maximum extinction angles ( $\gamma \wedge C$ ) are around  $16^\circ$ .

Seventy eight amphibole analyses have been obtained from 11 of the meta-dolerites of the Conwy Valley (Figure 4.19.1) including 24 analyses of the amphiboles which overgrow clinopyroxene and 54 analyses of the new acicular amphiboles (16 amphibole analyses are presented in Appendix 5). The amphibole analyses have been recalculated to a general structural formula of  $AX_2 Y_5 Z_8 O_{22} (OH)_2$ ; where X = Ca, Na and K, Y = Mg,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Al^{VI}$  and Ti, and Z = Si, and  $Al^{IV}$  (Borg, 1967) on the anhydrous basis of 23 oxygens. This assumes that the Z sites are filled with Si and Al and the remaining Al is allocated to octahedral sites (M2). The analyses reveal significant variation in the Fe, Mg and Al cations with relatively good negative correlation ( $r = -.85$ ) between Fe and Mg indicating substitution between these ions. Very low values of Ti (not detected), Na (detected in 3 analyses) and K (detected in 2

FIGURE 4.18.1. Epitaxial overgrowth of actinolite on a relict clinopyroxene crystal, sample 168J (Moe1 Siabod). XP. X14.

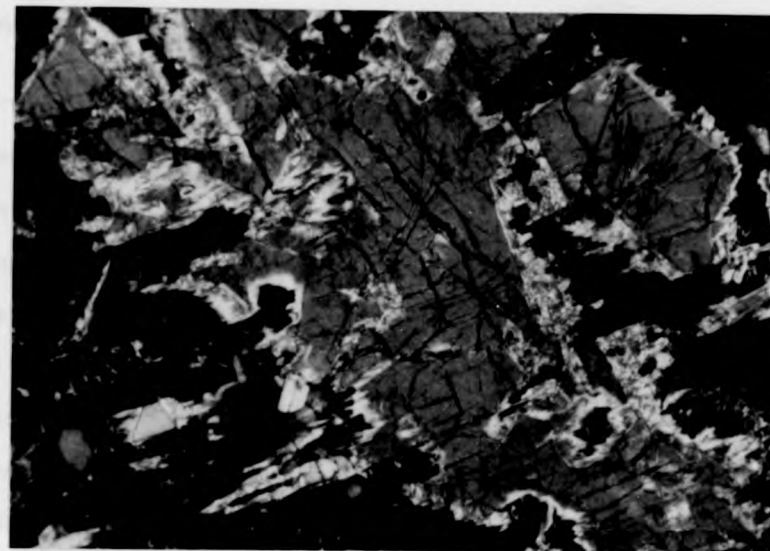


FIGURE 4.18.2. Acicular actinolite occurring with chlorite in an interstitial alteration site, sample 168J (Moe1 Siabod). XP. X85.

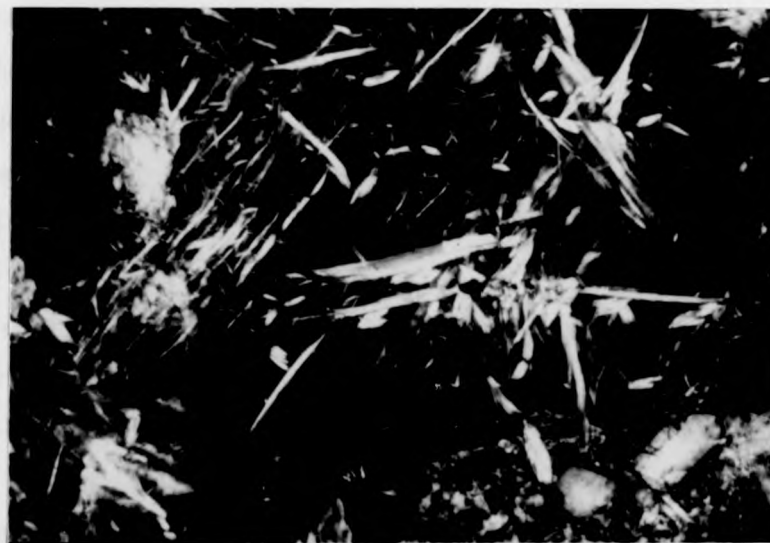


FIGURE 4.18.1. Epitaxial overgrowth of actinolite on a relict clinopyroxene crystal, sample 168J (Moel Siabod). XP. X14.

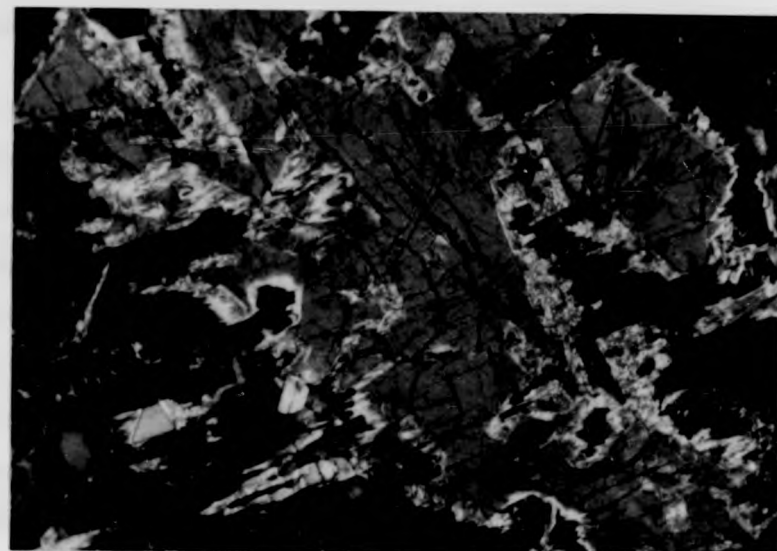


FIGURE 4.18.2. Acicular actinolite occurring with chlorite in an interstitial alteration site, sample 168J (Moel Siabod). XP. X85.



FIGURE 4.18.1. Epitaxial overgrowth of actinolite on a relict clinopyroxene crystal, sample 168J (Moe1 Siabod). XP. X14.

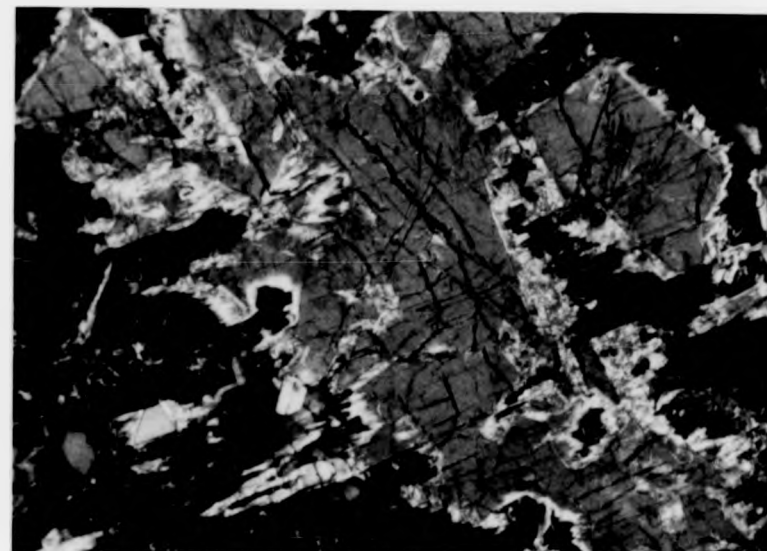
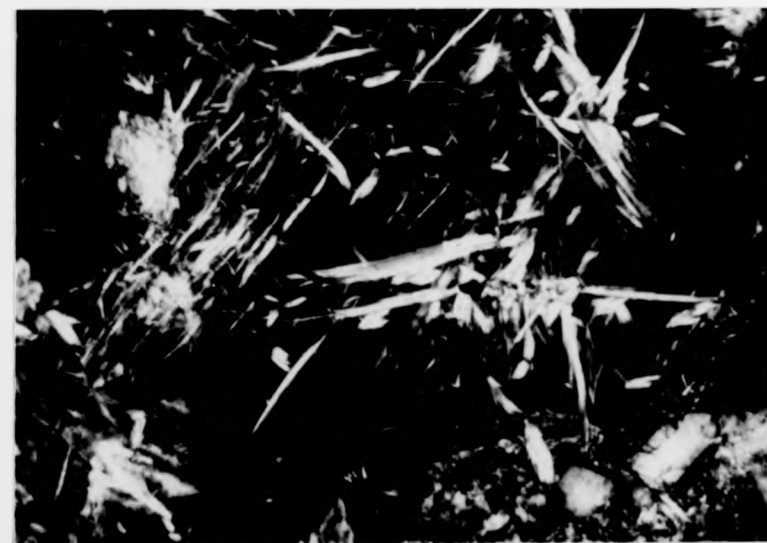


FIGURE 4.18.2. Acicular actinolite occurring with chlorite in an interstitial alteration site, sample 168J (Moe1 Siabod). XP. X85.



analyses) are typical of actinolites produced during the lowest grades of metamorphism (Coombs et al., 1976).

Iron and magnesium are highly variable in actinolites from different samples but from the same sample the Fe/Mg ratio is relatively constant (Figure 4.19.1). The range in inter- and intra-sample Al is from approximately 0.1 - 0.82 cations in the formula. No significant systematic difference in chemical composition exists between acicular actinolite and the amphibole overgrowing relict clinopyroxene. The variation in Fe and Mg is thought to reflect the influence of host rock chemistry with good correlation ( $r = .88$ ) between host rock  $FeO^*/FeO^* + MgO$  and actinolite  $Fe/Fe + Mg$  (Figure 4.19.2). Recently Rowbotham (1984, pers. comm.) has found that a correlation exists between actinolite orientation and Al content. It is possible that much of the variation in Al observed between the individual actinolite crystals present within a sample could be a reflection of this relationship.

These observations are in close agreement with those of Kawachi (1975), Coombs et al., (1976) and Bevins and Rowbotham (1983) who describe strong host rock chemical control on the Fe/Mg ratios of actinolites and small, but highly variable, amounts of Al in actinolites from areas of low-grade metamorphism. Kawachi (1975) attempted to relate Al content to metamorphic grade with the lowest grade actinolites (pumpellyite - actinolite facies) being less aluminous than those developed at higher grade (biotite zone of the greenschist facies and the epidote-glaucophane sub-facies). This relationship has also been observed in other areas of greenschist to amphibolite facies metamorphism with the development of relatively more aluminous actinolitic amphiboles in higher grade samples (Graham, 1974). However, due to the highly variable Al contents of actinolite in the Conwy Valley it is felt that factors other than metamorphic grade (for example, amphibole orientation) may also be an

FIGURE 4.19.1. Al - Fe - Mg for actinolitic amphiboles from the Conwy Valley.

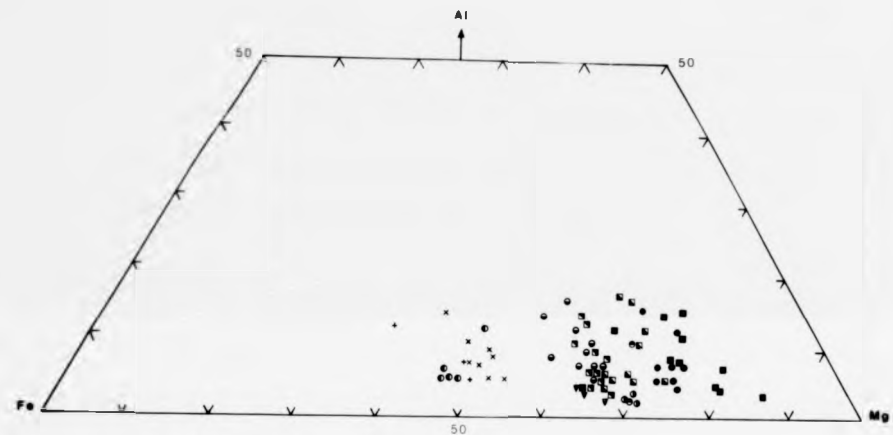
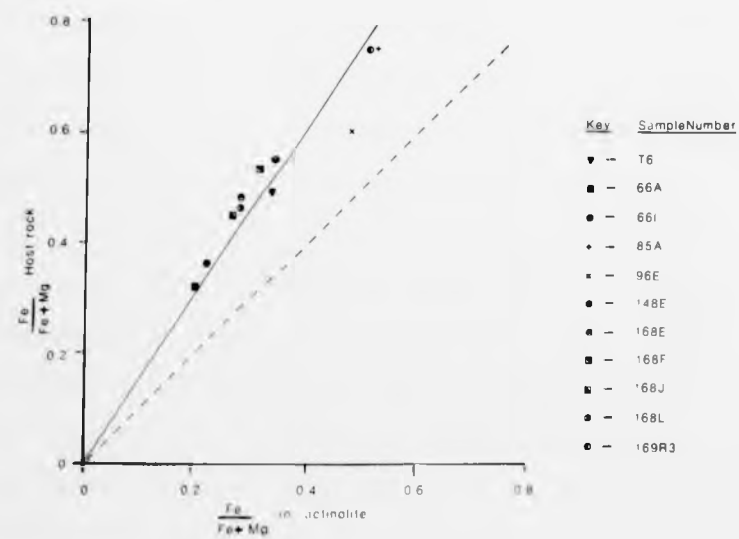


FIGURE 4.19.2. Host rock Fe/Fe+Mg vs actinolite Fe/Fe+Mg in the Conwy Valley.



important influence on the Al content of actinolites. The broad chemical similarity of epitaxial and acicular amphiboles indicate that both may be metamorphic in origin.

#### 4.3.8. White mica

White mica has been recognised in 129 of the meta-dolerites and occurs throughout northern Snowdonia. It occurs as small flakes within albitised plagioclase or, rarely, within the groundmass. The amount varies considerably with several samples being particularly rich in white mica (for example, samples 66K, 104E and 104F).

The white mica is colourless and of low relief. In a few samples a very faint green or yellow tinge is evident. The interference colours are occasionally relatively low for white mica but the flakes are often very thin.

Thirty analyses of white mica have been obtained from 6 of the meta-dolerites of the Conwy Valley (16 white mica analyses are presented in Appendix 5). Although white mica is abundant it has proved difficult to obtain a large number of reliable analyses due to the very small grain size. The general formula for dioctahedral micas is  $X_2 Y_4 Z_8 O_{20} (OH,F)_4$ ; where X is mainly Na, K or Ca, Y is mainly Al, Mg or Fe and Z is mainly Si or Al (Deer et al., 1962). Mineral recalculations have been made on the anhydrous basis of 22 oxygens and assume that the Z sites are filled (8 cations) with Si and Al. Residual Al together with Fe and Mg are allocated to the octahedral sites. It has been assumed that all the iron is present as  $Fe^{2+}$ . Coombs et al., (1976) show that a large amount of  $Fe^{3+}$  often occurs in white micas. This could possibly account for the consistently high cation totals in the octahedral sites. Rarely trace amounts of Na and Ca were detected in the white micas which probably reflects admixed plagioclase feldspar.

FIGURE 4.20. Al - Fe - Mg for the phengitic white micas from the Conwy Valley. Also shown is the compositional field of white mica from New Zealand (Kawachi, 1975).

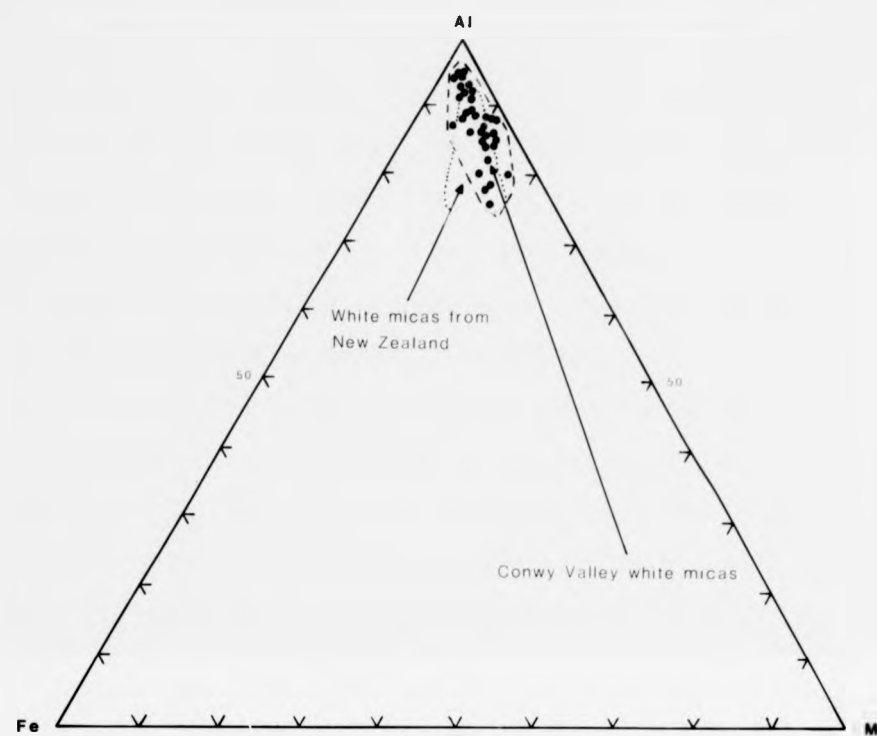
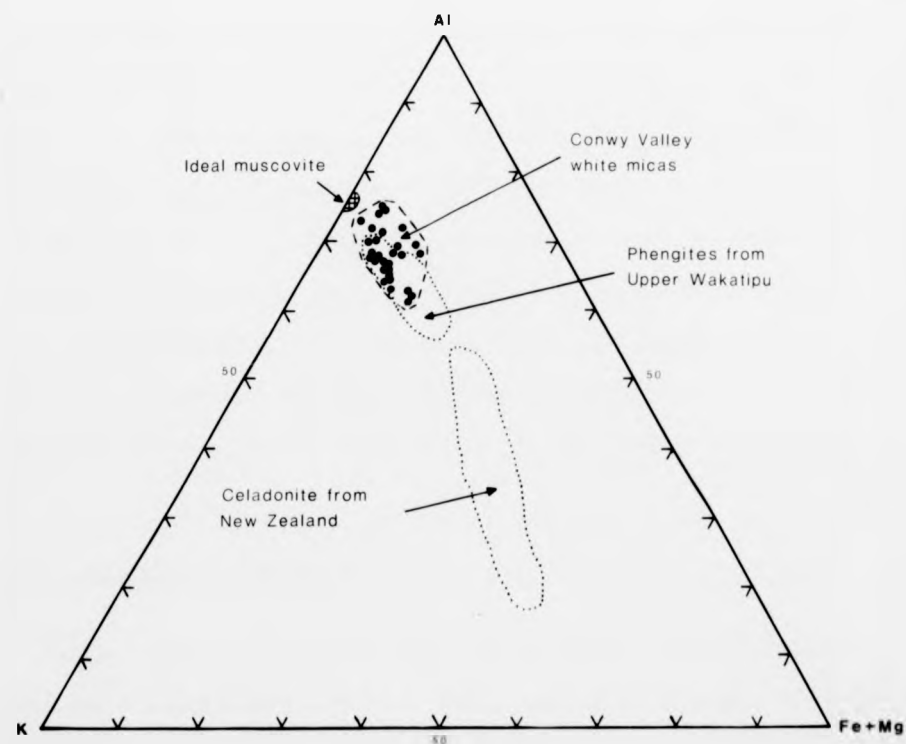


FIGURE 4.21. Al - K - Fe + Mg for the phengitic white micas from the Conwy Valley. Also shown are the compositional fields of celadonites from the Hokonui Hills, New Zealand (Boles and Coombs 1977) and Phengites from Upper Wakatipu (Kawachi, 1975).





In many of the analyses, Si contents are high, often exceeding 6.5 Si cations per  $O_{20}(OH)_4$ . Also the tetrahedral Si : Al ratio, ranging from 3.50 - 5.49, is significantly higher than the 3 : 1 ratio of true muscovites (Deer et al., 1962). Significant amounts of Fe and Mg are also present in the octahedral sites (up to 1.15 cations per  $O_{20}(OH)_4$ ). These observations, taken together, indicate that much of the white mica from the Conwy Valley is phengitic, in common with white micas from other low-grade terrains. Using the formula  $Fe + Mg / \text{total octahedral cations} \times 100$  to calculate the celadonite content it is possible to quantify the phengitic substitution of celadonite ( $K(Mg, Fe^{2+})(Al, Fe^{3+})Si_4O_{10}(OH)_2$ ) into muscovite (Kawachi, 1975; Coombs et al., 1976).

The Conwy Valley phengitic micas are plotted on AFM and Al - K - Fe + Mg diagrams (Figures 4.20 and 4.21) together with fields for phengites from Upper Wakatipu and Otago (Kawachi, 1975) and zeolite facies celadonites from the Hokonui hills (Boles and Coombs, 1977). The compositional field of phengitic micas from throughout the Welsh basin (Bevins and Rowbotham, 1983) is very similar to that displayed by the Conwy Valley micas. Clearly the compositional fields of phengitic micas from the Conwy Valley and Upper Wakatipu are also very similar. The celadonite content of the Conwy Valley micas is rather variable (even within the same sample) and ranges from 6.3 - 39.6%, with a mean of 16.5%. For comparison the Upper Wakatipu white mica celadonite content is slightly higher, ranging from 12 - 44% and with a mean of 24%.

#### 4.3.9. Plagioclase feldspar

Primary igneous plagioclase has suffered large scale albitisation during the low-grade metamorphism. Relict calcic plagioclase is rarely preserved (Section 4.2.2). Albitised feldspars are often cloudy and

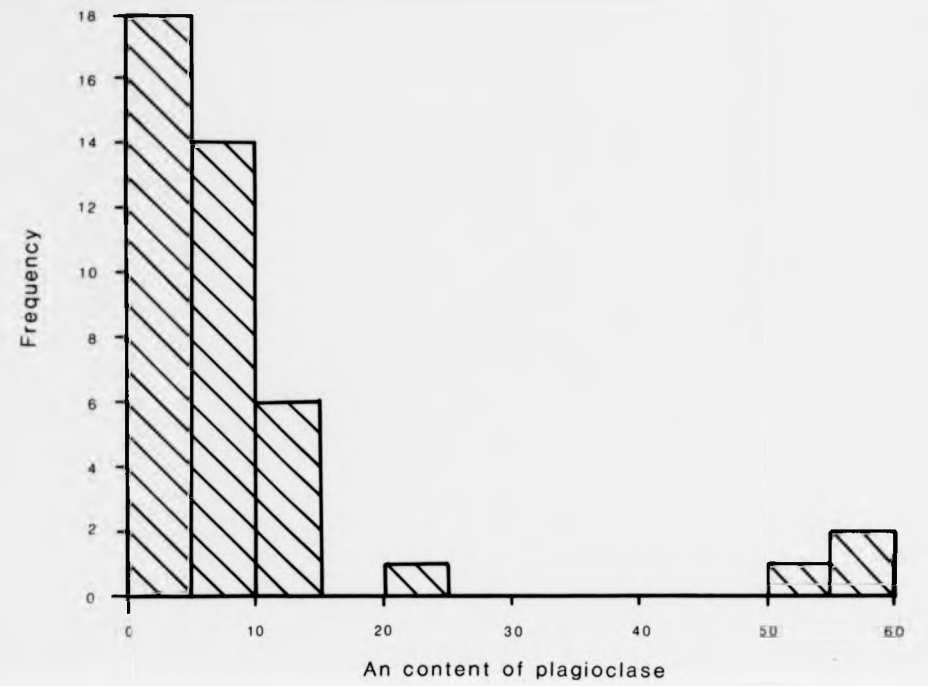
provide one of the major alteration sites (Chapter 3).

There have been 45 plagioclase analyses obtained from 14 of the meta-dolerites from the Conwy Valley (12 plagioclase analyses are presented in Appendix 5). Mineral recalculations have been made on the basis of 8 oxygens in the formula unit. The analyses show marked variation in the relative proportions of the major cations Al, Si, Na and Ca (Figure 4.22.1) indicating that the process of albitisation has not been completed, an observation consistent with those made elsewhere in the Welsh basin (Bevins and Rowbotham, 1983). In most samples the anorthite ( $\text{Ca Al}_2 \text{Si}_2 \text{O}_8$ ) component of the plagioclase feldspar is less than 10% indicating that most plagioclase is albite ( $\text{Na Al Si}_3 \text{O}_8$ ). However, in several samples the average An content is much higher ( $\text{An}_{49-59}$ ) indicating a plagioclase of labradoritic composition. These latter plagioclases are thought to be igneous relicts. In a few samples there is a large range in An content between individual crystals (Figure 4.22.2), for example, in sample 148E a range between  $\text{An}_{22}$  and  $\text{An}_5$  exists. This further indicates that albitisation in the Conwy Valley is rather variable, not only on the large scale (between samples) but on the smaller scale (between the individual plagioclase crystals within a sample).

#### 4.3.10. Alkali feldspar

Alkali feldspar has been identified in only one sample of meta-dolerite (sample 168E), and this has been confirmed by microprobe analysis. The alkali feldspar is probably adularia and occurs as anhedral patches associated with epidote, chlorite and actinolite in the interstitial alteration sites or as an alteration product of original calcic plagioclase. The original calcic nature of the feldspars is indicated by the frequent development of secondary Ca - Al silicates

FIGURE 4.22.1. A histogram showing the composition of plagioclase from the Conwy Valley.



4.22.2. Variation in albitisation within samples from the Conwy Valley.

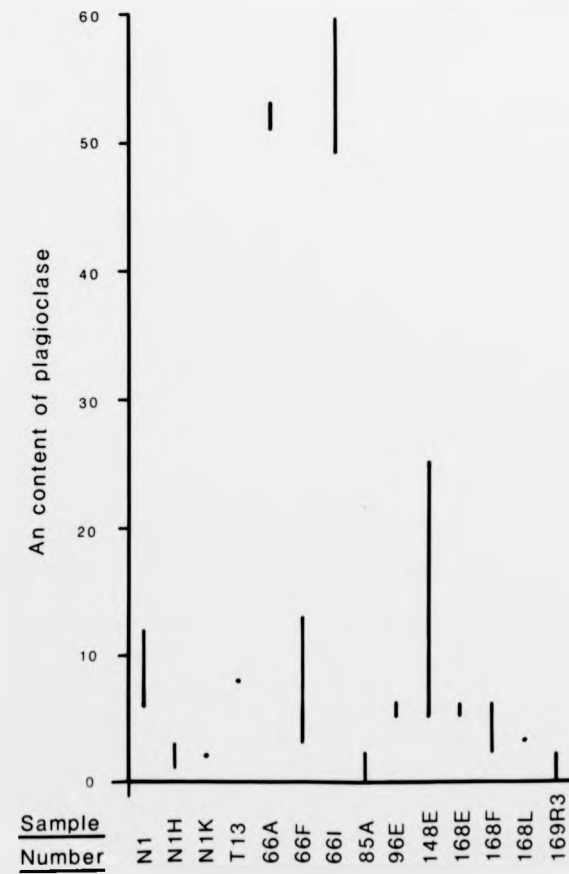
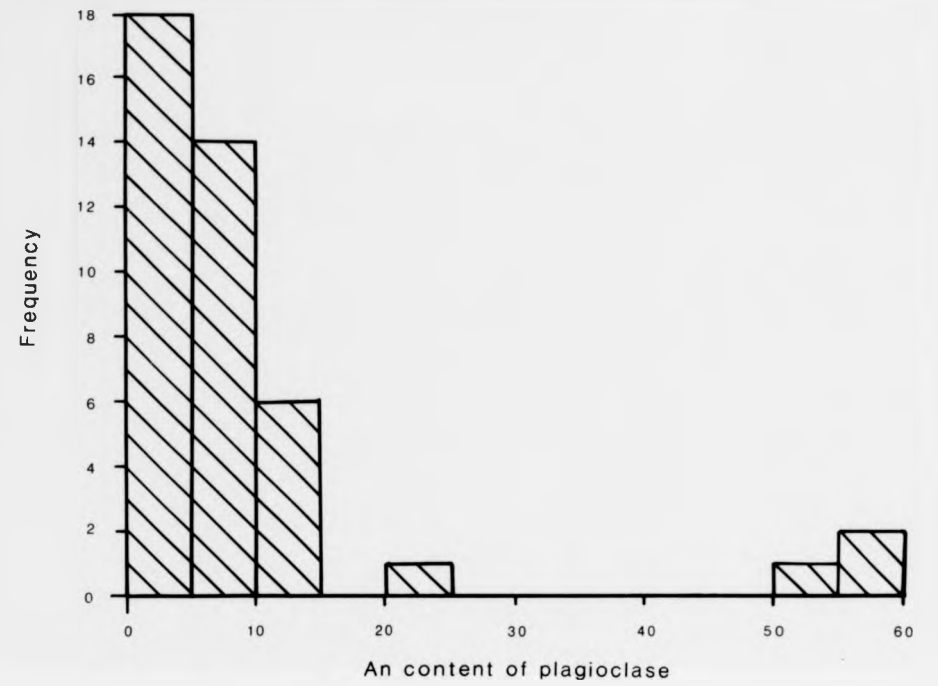


FIGURE 4.22.1. A histogram showing the composition of plagioclase from the Conwy Valley.



4.22.2. Variation in albitisation within samples from the Conwy Valley.

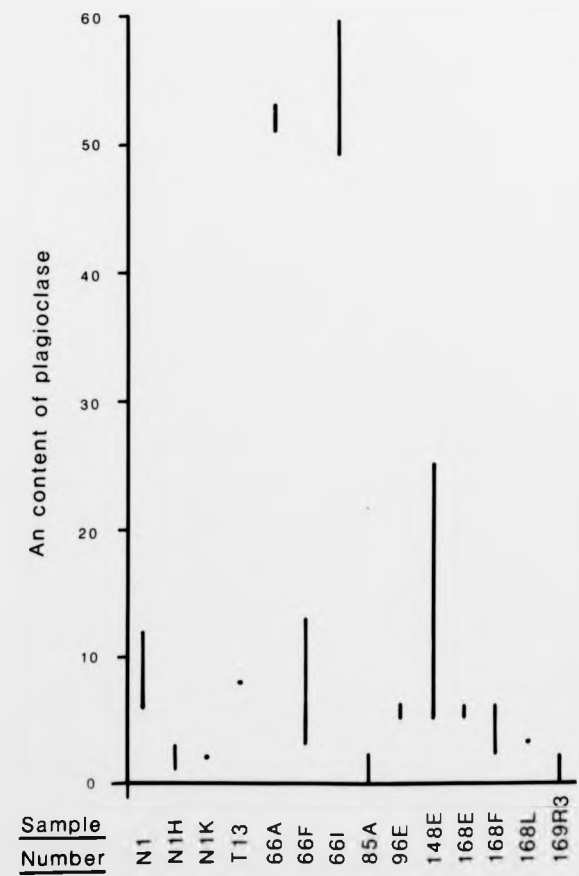


FIGURE 4.23. Chlorite, quartz and (minor) ferristilpnomelane  
infilling vesicles, sample 179C (Moei Siabod).  
XP. X14.

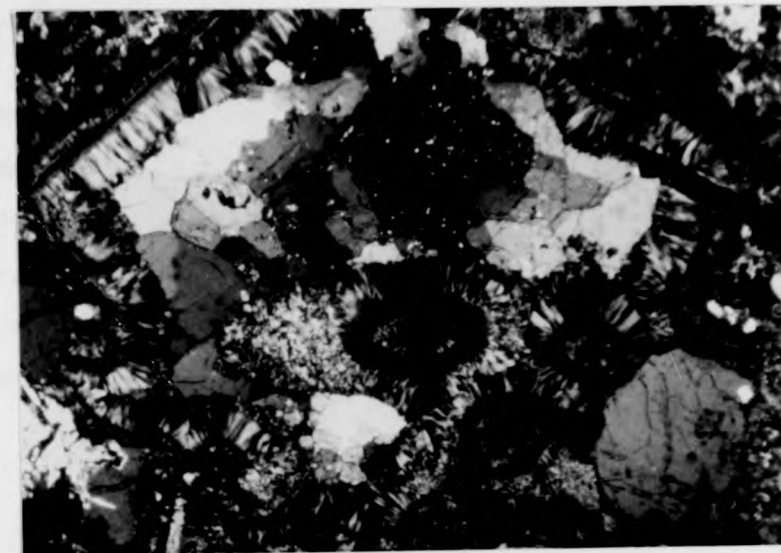
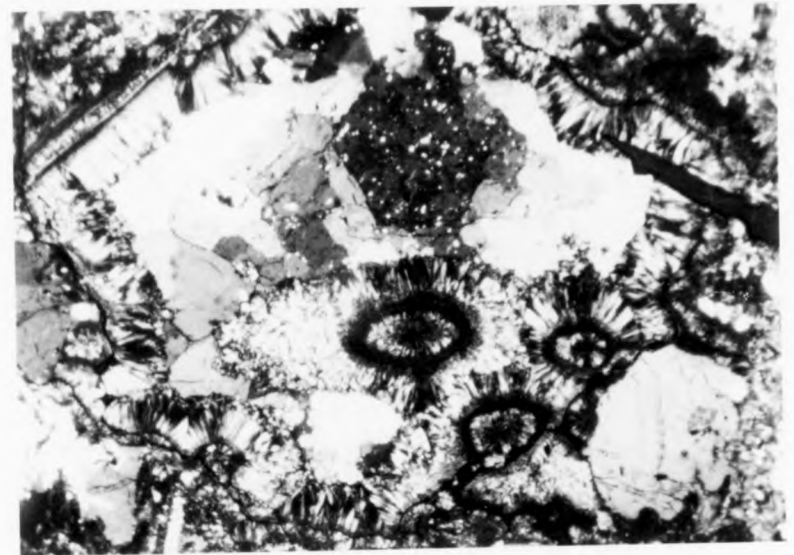


FIGURE 4.23. Chlorite, quartz and (minor) ferristilpnomelane  
infilling vesicles, sample 179C (Moel Siabod).  
XP. X14.



within the feldspars. In sample 168E alkali feldspar and the more typical albitised plagioclase coexist.

Three analyses of the alkali feldspar were obtained and are presented in Appendix 5. The orthoclase content of these feldspars is very high (or = 95 - 99%). They all contain small amounts of Ca and Fe, however, in only one analysis was any Na detected. Bevins and Rowbotham (1983) also record the presence of rare alkali feldspar in the Welsh meta-dolerites recognising both microcline and adularia.

#### 4.3.11. Quartz

Quartz is present in almost all of the meta-dolerites from northern Snowdonia but usually in small amounts. Occasionally it is present in larger amounts, most notably in the contact zones of many of the larger sills where it can occur as small veins. Most characteristically quartz occurs as small rounded inclusions scattered throughout the groundmass. Occasionally it is found infilling vesicles in association with chlorite (Figure 4.23), for example, on Moel Siabod (sample 179C). Larger quartz grains often display undulose extinction.

No analyses of quartz have been obtained.

#### 4.3.12. Calcite

Calcite is frequently developed in the meta-dolerites of northern Snowdonia but usually in only small amounts. Locally calcite is more abundant particularly in the fine grained margins of many of the larger sills where much of the groundmass may be calcitic. Calcite occurs as either isolated anhedral patches within the groundmass or as small patches or veins within albitised plagioclase.

No analyses of the carbonate phase have been obtained.

#### 4.4. Chemical equilibrium

In Chapter 3 it was shown that there is significant evidence for some textural disequilibrium within the meta-dolerites of northern Snowdonia. With the availability of mineral chemistry data it is possible to investigate equilibrium more rigorously. Features that might indicate an approach towards chemical equilibrium include:- i) a lack of chemical zoning, ii) similar compositions for all crystals of a specific secondary phase within a sample, and, iii) sympathetic chemical variation between the constituent secondary minerals in a sample.

In Section 4.3.3. the epidotes were examined in some detail and microprobe analysis confirmed the optical observation that many of them are continuously zoned from Fe-rich cores to Fe-poor rims. The presence of such zoning might indicate possible chemical disequilibrium, or at least a situation where epidote composition progressively changes as metamorphic conditions alter, with the earlier formed epidote protected from reaction by a layer of new epidote in equilibrium at the new pressure, temperature,  $fO_2$  and fluid conditions. If this is the case then only the composition of the outer shell need be in chemical equilibrium with the finally formed metamorphic assemblage, with the more Fe-rich cores being isolated from the metamorphic system (Zen, 1974). Hence the presence of zoned phases need not necessarily reflect widespread chemical disequilibrium.

Another feature indicative of chemical disequilibrium is the marked chemical variation observed between different crystals of the same secondary phase. Extreme examples of this have already been mentioned, most obviously that of markedly different epidote compositions in the interstitial and plagioclase alteration sites. Detailed microprobe



analysis reveal that considerable chemical inhomogeneity exists between many crystals of specific secondary phases within the area of a thin section, examples include:- i) variable Al-Fe-Mg compositions of white micas, ii) marked variation in the Al contents of actinolites irrespective of whether they are acicular or form epitaxial overgrowths around pyroxene. In Section 4.3.7. it was shown that much of this variation could reflect differences in orientation of the amphibole crystals (Rowbotham, 1984, pers. comm), iii) marked variation in the PS content of epidotes even where optical zoning is not evident, and iv) the extremely variable An content of plagioclase feldspars reflecting the incomplete nature of the process of albitisation. All these chemical inhomogeneities are problematic if the dolerites are assumed to have been in chemical equilibrium with the fluid throughout the period of metamorphism.

Kawachi (1975) and Coombs et al., (1976) describe similar chemical variation to that outlined above. In addition they have also observed systematic variation in Fe : Mg ratios between coexisting chlorites, actinolites and pumpellyites which they interpret as an approach towards chemical equilibrium for Fe and Mg in these secondary phases. The mean data for chlorites and actinolites from the Conwy Valley is plotted on an AFM diagram (Figure 4.24.1) and mineral pairs from the same sample are indicated by tie lines. In a system in chemical equilibrium the partitioning of Al, Mg and Fe between phases should be systematic and tie lines should not cross. In general tie lines are sub-parallel (Figure 4.24.1) indicating a degree of chemical equilibrium, however, two sets of tie lines cross which indicates possible chemical disequilibrium in these samples. The possibility that this disequilibrium is related to either scale or to the nature of the amphibole can be explored by the examination of pairs of analyses from i) acicular actinolite and chlorite, ii) epitaxial actinolite and chlorite, and, iii) actinolite and

FIGURE 4.24.1. Al - Fe - Mg for actinolite and chlorite occurring together in the same sample.

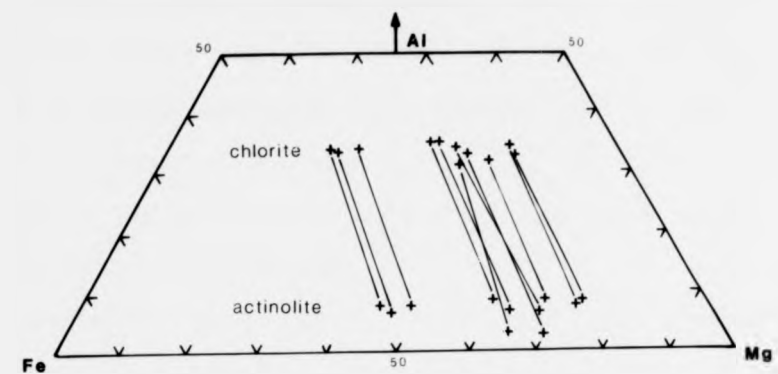


FIGURE 4.24.2. Al - Fe - Mg for acicular actinolite and chlorite occurring together in the same sample.

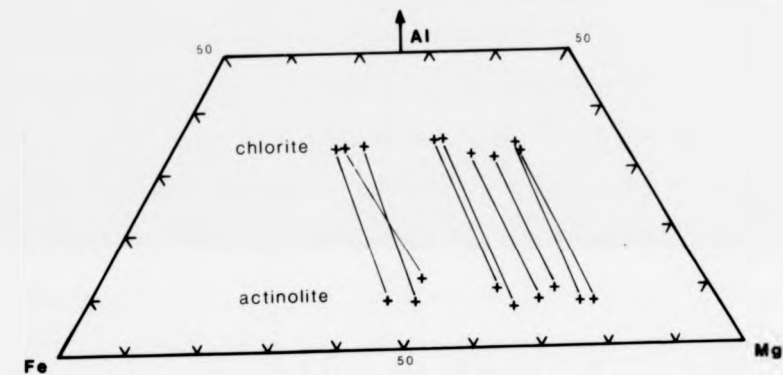


FIGURE 4.24.3. Al - Fe - Mg for epitaxial actinolite and chlorite occurring together in the same sample.

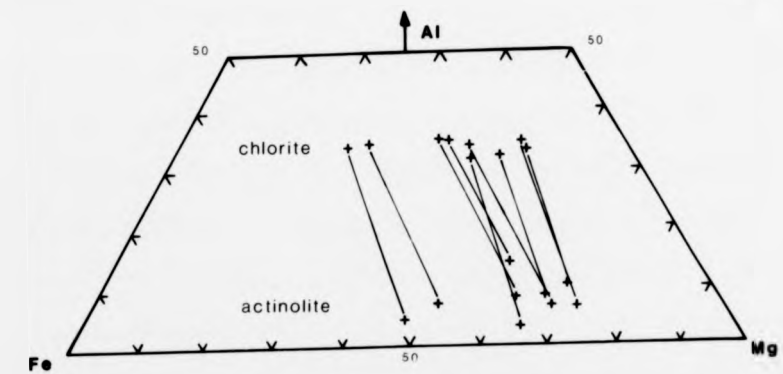
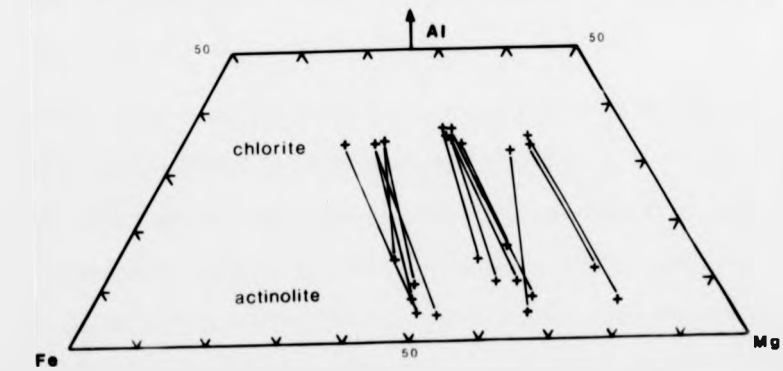


FIGURE 4.24.4. Al - Fe - Mg for actinolite and chlorite occurring in actual physical contact.



chlorite in physical contact (Figures 4.24.2., 4.24.3 and 4.24.4). In all these cases most of the tie lines are again sub-parallel, however, a minority of the tie lines cross which probably indicates some chemical disequilibrium even on a relatively small scale. Some of the variation in the angle of the tie lines may reflect the influence of amphibole orientation on composition (above).

If pumpellyite, chlorite and actinolite which occur together in the same sample are considered then the same sort of relationship exists with there being sympathetic variation in phase chemistry in a majority of samples (Figure 4.25.1). In Figure 4.25.2 mean epidote, pumpellyite and prehnite compositions are plotted on a  $2\text{Fe}^{3+} - 2\text{Al} - \text{Ca}$  diagram and minerals from the same sample are joined by tie lines. Again there is broadly sympathetic variation in mineral chemistry but with a minority of crossing tie lines. This is most clearly seen in sample T13 (from Tal-y-Fan) where Fe-rich epidote occurs with Fe-rich prehnite but the associated pumpellyite is relatively Fe-poor. In Figure 4.25.3 the effects of epidote zoning are shown on a  $2\text{Fe}^{3+} - 2\text{Al} - \text{Ca}$  diagram. The phase chemistry data indicates a systematic relationship between the compositions of coexisting secondary minerals in a majority of examples. However, some chemical disequilibrium is indicated with some crossing of compositional tie lines on all the relevant diagrams (Figures 4.24.1-4 and 4.25.1-3). In all the above examples, where compositional tie lines are seen to cross, there does not appear to be any relationship between crossing tie lines and the relative location of the samples involved.

The distribution coefficients ( $K_D$ ) for Mg/Fe in chlorites and actinolites from the Conwy Valley have been calculated. In the literature a systematic relationship has been observed between Mg/Fe in actinolite and Mg/Fe in chlorite with a  $K_D$  of 1.72 (Kawachi, 1975, Coombs et al., 1976). The  $K_D$  values for Conwy Valley samples have been determined (Figure 4.26.1) and show quite a large range of values (1.72 - 1.10). In order to eliminate the possibility of disequilibrium on the scale of

FIGURE 4. 25.1. Al-Fe-Mg for pumpellyites, chlorites and actinolites occurring together in the same thin section.

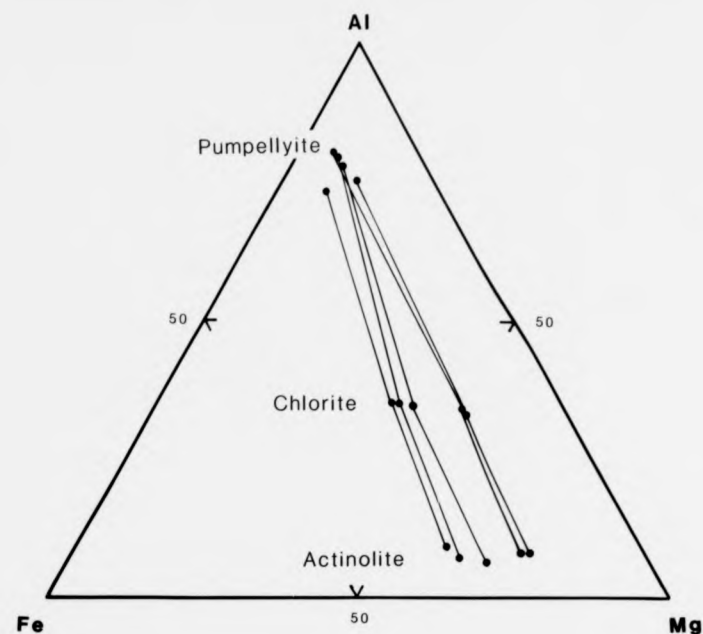


FIGURE 4. 25.2. A  $2Al-2Fe^{3+}-Ca$  diagram showing the mean compositions of epidotes, pumpellyites and prehnites occurring together in the same thin section.

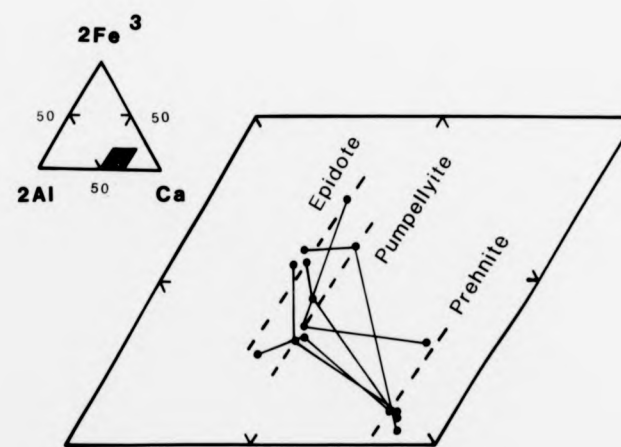


FIGURE 4. 25.3. A  $2Al-2Fe^{3+}-Ca$  diagram showing the effects of epidote zoning on compositional tie lines.

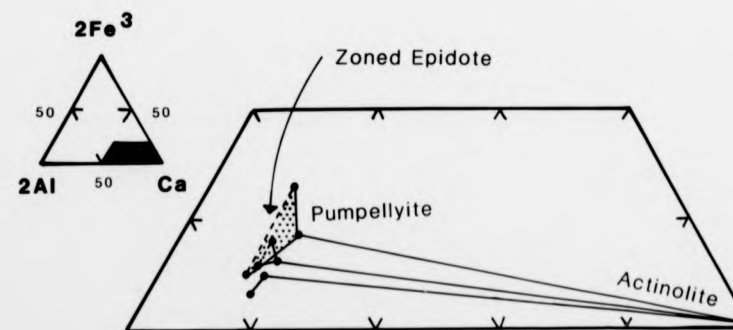


FIGURE 4.26.1. Fe/Fe+Mg in chlorites and actinolites occurring together in the same sample.

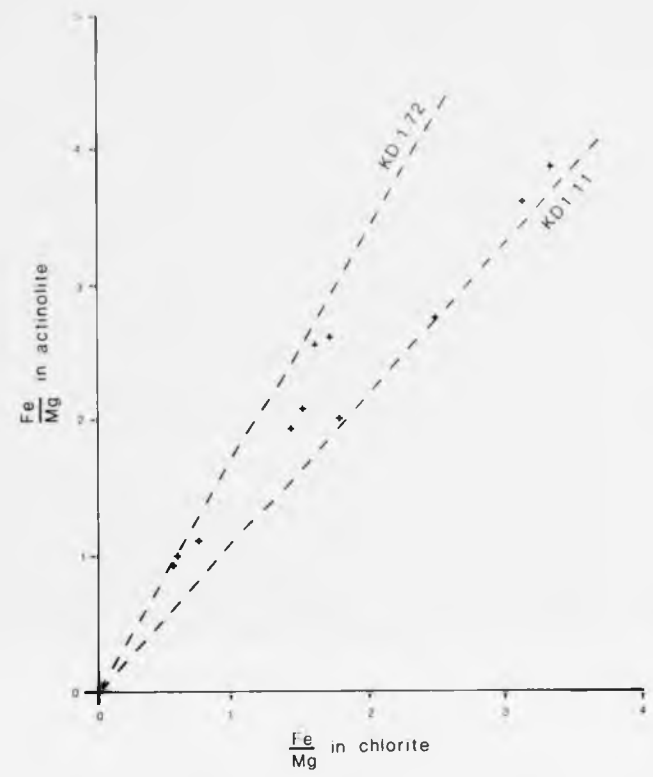
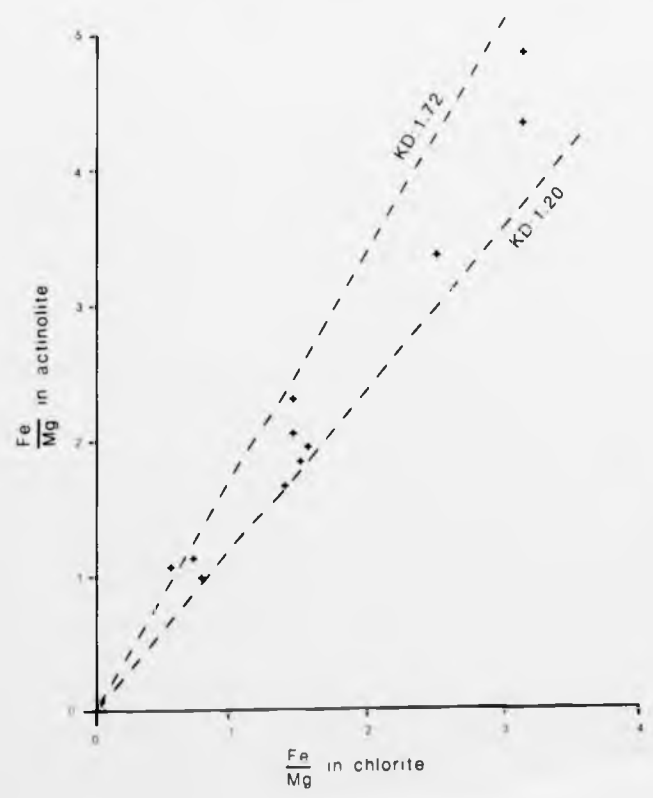


FIGURE 4.26.2. Fe/Fe+Mg in chlorites and actinolites occurring in actual physical contact.



a thin section the Mg/Fe for chlorites and actinolites in physical contact have also been plotted (Figure 4.26.2). The same pattern is again observed with the  $K_D$  ranging from  $> 1.72 - 1.20$ .

From the above discussion, and the petrographic evidence of Chapter 3, it would appear that although there is much evidence indicating an approach towards equilibrium, in many of the samples of northern Snowdonia there is also significant evidence suggesting an element of petrographic and chemical disequilibrium. Petrographic and chemical evidence indicative of equilibrium includes adherence to the phase rule by the majority of the samples, the general parallelism of compositional tie lines and sympathetic variation in the  $Fe^{3+}/Fe^{2+} + Al$  ratios of coexisting phases. Evidence indicating some disequilibrium includes the presence of relict igneous phases, violation of the phase rule by a number of samples, compositional inhomogeneity between different crystals of specific secondary phases and the crossing of compositional tie lines in a minority of samples.

#### 4.5. Discussion

The petrographic observations and phase chemistry analyses should allow some quantification of metamorphic conditions but considering the problems of disequilibrium, outlined above, care should be exercised in the interpretation of the secondary assemblages.

The widespread development of hydrous Ca - Al silicates indicates that the metamorphic fluid was  $H_2O$  rich containing little  $CO_2$  (Coombs et al., 1970; Zen, 1974; Glassley, 1974; Brown, 1977). High  $\mu_{CO_2}$  quickly leads to the suppression of minerals such as pumpellyite with minerals like calcite, chlorite and epidote crystallised instead. Coombs et al. (1976) examined low-grade mineral reactions in a mixed  $CO_2 - H_2O$  fluid and calculate that  $X_{CO_2}$  in the fluid must have been less than about 0.02% for pumpellyite bearing assemblages from Switzerland.

The presence of zoned epidotes from Fe-rich cores to Fe-poor rims and the  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Al}$  contents of coexisting epidotes, pumpellyites and prehnites yield valuable information concerning the metamorphic environment. Nakajima et al. (1977) and Liou et al. (1983) argue that as metamorphic grade increases  $\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Al}$  in prehnite, pumpellyite and epidote will decrease (for rocks of similar composition and at constant  $f\text{O}_2$ ). The analysed prehnites from the Conwy Valley generally display very low Fe contents suggesting that these are high temperature prehnites crystallised near the upper temperature limit of their stability field. The epidote zoning may indicate either an increase in temperature, with initial lower temperature Fe-rich epidote giving way progressively to higher temperature Fe-poor epidote, or a change in fluid composition during epidote crystallisation (Bird and Helgeson, 1981). The trend from Fe-rich to more aluminous pumpellyites southwards within the Conwy Valley might indicate a gradual increase in temperature southwards. These observations collectively indicate that temperature was rather higher in the south and rather lower in the north and that temperatures increased throughout recrystallisation.

Although pumpellyite and actinolite frequently occur in the same sample there is some evidence that they may not be in textural equilibrium as they are never seen to physically touch and usually occupy different alteration sites (actinolite in the interstitial alteration sites, pumpellyite in the plagioclase alteration sites). Thus it might be wrong to ascribe these rocks to the pumpellyite-actinolite facies even though they contain the diagnostic pumpellyite + actinolite assemblage. The presence of coexisting prehnite and pumpellyite, occasionally in physical contact, in the northern Conwy Valley is diagnostic of the prehnite-pumpellyite facies. The presence of coexisting clinozoisite and actinolite in the central Conwy Valley is diagnostic of the lower greenschist facies. Hence there is reliable evidence for prehnite-

pumpellyite and lowest greenschist facies metamorphism in the Conwy Valley with the occasionally developed pumpellyite-actinolite assemblage possibly reflecting some disequilibrium on the scale of the thin section.

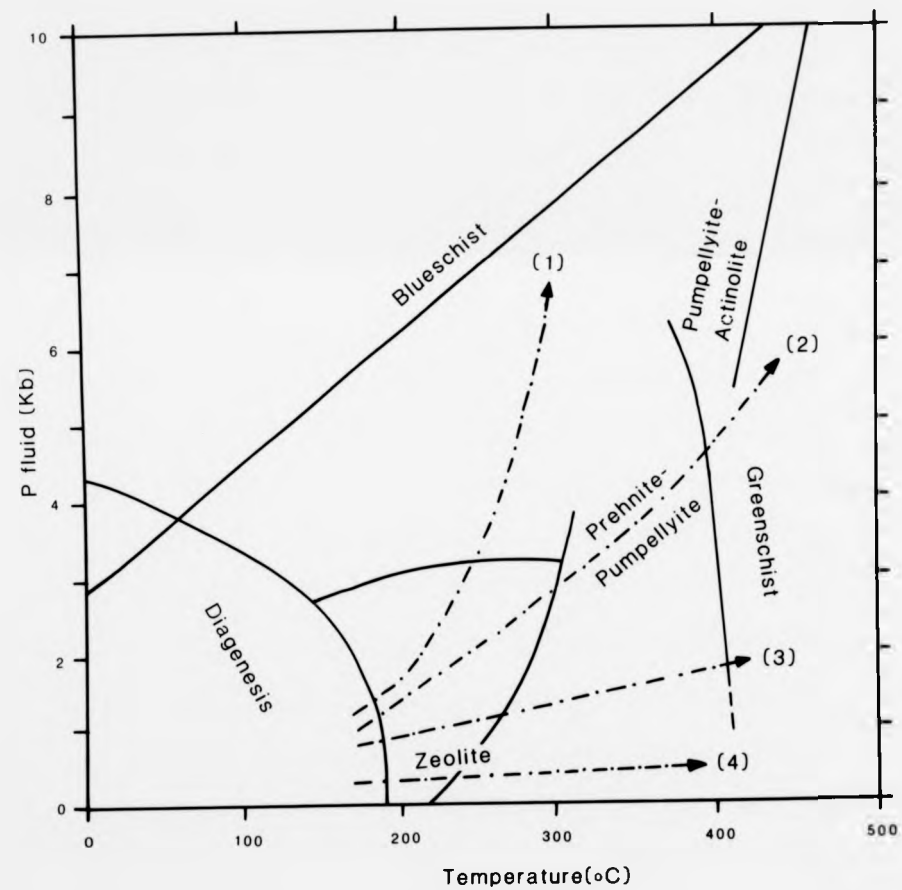
Figure 4.27 is from Liou (1971b) and shows the approximate pressure/temperature fields of low-grade metamorphic facies. The presence of prehnite-pumpellyite and lower greenschist facies assemblages, in the absence of a recognisable pumpellyite-actinolite facies, represents relatively low pressures of metamorphism as the stability field of the pumpellyite-actinolite facies is pressure dependent and decreases in extent rapidly as pressure falls (Hashimoto, 1972; Nakajima et al., 1977). The absence of any characteristic high pressure phases such as lawsonite, glaucophane and aragonite also indicates intermediate or low pressure metamorphism with total pressures < 4Kb.

Liou (1971b), Schiffman and Liou (1980) and Liou et al. (1983) examine phase equilibria amongst many of the diagnostic secondary Ca-Al silicates. Despite the evidence for some disequilibrium in the meta-dolerites of the Conwy Valley, careful application of these equilibrium studies can provide valuable information. Schiffman and Liou (1980) experimentally show that the boundary of the prehnite-pumpellyite facies with the greenschist facies occurs between 375°C at 5 Kb and 275°C at 1 Kb, based on the disappearance of Mg-Al pumpellyite. They also note that the presence of Fe within the pumpellyite will reduce its upper temperature stability. It would appear, therefore, that metamorphic temperatures in the pumpellyite bearing areas of the northern Conwy Valley were significantly less than 375°C. Relative temperatures in the central and southern Conwy Valley were probably slightly higher than in the north.

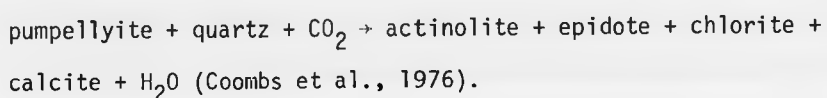
In central northern Snowdonia pumpellyite is virtually absent, possibly indicating relatively high temperatures. However, the associated epidotes are invariably Fe-rich and suggest a lower, rather



**FIGURE 4.27.** The approximate pressure/temperature fields of low-grade metamorphic facies, from Liou (1971b).



than a higher, temperature of metamorphism. The one example of pumpellyite from central northern Snowdonia is a dark green, presumably Fe-rich variety displaying no sign of breakdown, and occurs in a typical meta-dolerite associated with pistacitic epidote, chlorite, albite and actinolite, again possibly suggesting lower, not higher, temperatures. It is possible that the composition of the fluid was important in determining the secondary mineral assemblage in central northern Snowdonia with the fluid being slightly more CO<sub>2</sub> rich thus preferentially suppressing pumpellyite and favouring the development of chlorite, epidote and calcite rich assemblages through a reaction such as:



The abundant needles of actinolite in northern Snowdonia are, on textural grounds, later than the chlorite and epidote with which they are frequently associated. The appearance of actinolite suggests minimum pressures of about 2.5Kb at temperatures of about 300°C (Zen, 1974). The late development of acicular actinolite might reflect somewhat higher pressures during late burial or deformation or the effects of relatively slow nucleation compared to the other secondary phases.

Evidence from the meta-dolerites indicates i) the presence of a H<sub>2</sub>O rich fluid during recrystallisation, ii) progressive increase in temperature throughout recrystallisation, iii) slightly higher temperatures in the central and southern Conwy Valley (lower greenschist facies) relative to the northern Conwy Valley (prehnite-pumpellyite facies). Evidence concerning metamorphic temperatures in central northern Snowdonia is in some respects contradictory, however, the balance of evidence indicates relatively low temperatures, and iv) relatively low pressures during metamorphism. These findings are in broad agreement with those of Bevins and Rowbotham (1983) who estimate maximum pressures and temperatures of 3.4Kb and 325°C for the central

areas of the Welsh basin based on the maximum stratigraphic thickness and an assumed geothermal gradient of  $25^{\circ}\text{C}$  per Km. Further discussion of the parameters of metamorphism in northern Snowdonia is postponed until Chapter 8 where the integrated data from all available sources is considered.

#### 4.6. Concluding remarks

Microprobe analysis of primary mineral phase chemistry supports the conclusion that the meta-dolerites of northern Snowdonia are fractionated tholeiitic sills which have subsequently suffered a low-grade metamorphism.

Detailed microprobe analysis of secondary mineral phase chemistry, in conjunction with detailed petrographic observations, allows some quantification of metamorphic conditions. In addition, a study of the phase chemistry has enabled the investigation of chemical equilibrium within the meta-dolerites. A degree of chemical equilibrium appears to have been attained in the Conwy Valley with sympathetic variation in the compositions of most secondary phases. However, evidence for significant disequilibrium also exists which corroborates the evidence of petrographic disequilibrium. The critical implication of these observations is that although phases occur in close proximity they need not, necessarily, represent stable equilibrium secondary mineral assemblages as different phases may have crystallised at different times and may indeed have formed under different pressure, temperature and fluid conditions.

From the available data the metamorphic fluid appears to have been largely  $\text{H}_2\text{O}$  with little or no  $\text{CO}_2$  present, particularly in the Conwy Valley. Temperatures significantly less than  $375^{\circ}\text{C}$  are envisaged in the Conwy Valley with relatively higher temperatures in the central and southern Conwy Valley (where pumpellyite is rare) compared to the northern Conwy Valley (where prehnite and pumpellyite are common).

Temperatures in central northern Snowdonia are rather more difficult to determine but, from the widespread development of unzoned, Fe-rich epidotes, are thought to have been similar to those of the northern Conwy Valley. Slight increase in temperature throughout recrystallisation is reflected through the zoned epidotes. The presence of acicular actinolite overgrowing chlorite and epidote might reflect kinetic factors or relatively slow nucleation, alternatively it may reflect the influence of increased pressures during late burial or Caledonian deformation. From the phase chemistry it would appear that actinolite is not always in equilibrium with the pumpellyite with which it occasionally occurs. Maximum pressures during metamorphism are thought to have been relatively low (< 4Kb) resulting in the development of prehnite-pumpellyite and lower greenschist facies assemblages in the absence of widespread stable pumpellyite-actinolite facies assemblages.