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ALTERATION OF BALLANTRAE LAVAS, AYRSHIRE

BY

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A thesis presented for the degree of M.Sc.



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## ABSTRACT

The Pinbain Block of the Ballantrae Complex has suffered a very low grade metamorphism, with the formation of albite-chlorite-sphene mineral assemblages. The base of the succession also has prehnite and pumpellyite, indicating the prehnite-pumpellyite facies, while the top is in the zeolite facies, and contains analcime. The temperature of the transition, based on mineral stabilities, is  $<190^{\circ}\text{C}$ . The metamorphism affected the sedimentary cover of the Ballantrae Complex, and it occurred without penetrative deformation, therefore it was a burial metamorphism.

Stable isotope studies show that the rocks were altered by large quantities of sea water, at a temperature of  $150\text{--}170^{\circ}\text{C}$ . This alteration resulted in the mobilisation of many of the chemical elements in the Pinbain Rocks, in a manner similar to that seen in experiments in which basalts are altered by sea water. Titanium, zirconium and yttrium remained immobile, and these elements can be used to identify the rocks as within-plate basalts.

Fluid inclusion studies show that some of the veins in the Pinbain Block were formed by a high-temperature hydrothermal fluid, which probably formed the ascending leg of a hydrothermal cell, which was replenished by downwards percolation of sea water.

The metamorphism probably occurred at the time of deepest burial, at the end of the Silurian, when Caledonian orogenesis may have raised the geothermal gradient and triggered the hydrothermal circulation.

CHAPTER ONE

INTRODUCTION

1.1 AIMS OF THE PROJECT

This thesis presents the results of research into the metamorphic geology of the Pinbain Lava Block, part of the Ballantrae Igneous complex in south-west Scotland, an early Ordovician ophiolite (Church & Gayer 1973; Dewey 1974). The research involved the use of several techniques in order to determine the timing and conditions of metamorphism, the mineralogical and chemical changes affecting the rocks, and the nature and quantity of the fluids present during the metamorphism. The Pinbain Melange and the Kilranny Conglomerate were studied in less detail, in order to compare and contrast them with the Pinbain Block.

1.2 GEOLOGICAL SETTING

### 1.2.1 Location

The Ballantrae Igneous Complex is situated on the southwest coast of Scotland, approximately 100 km south-west of Glasgow (fig 1.1). It lies just to the north of the Southern Uplands, on the edge of the Midland Valley.

### 1.2.2 Tectonic Setting

The Ballantrae Complex is part of the Scottish paratectonic Caledonides, an area made up of a number of terranes whose relationships have been discussed by Bluck (1985). Each terrane has a different character, and they are divided from each other by major tectonic boundaries. These boundaries may be faults along which major displacements have occurred, so that the present relationship between the terranes is purely structural in nature.

The Ballantrae Complex lies on the southern edge of the Midland Valley, an area now covered largely by upper Palaeozoic rocks. The basement of the Midland Valley is probably similar to the Lewisian of north-west Scotland, as indicated by seismic evidence (Bamford et al. 1977), and by the occurrence of granulite xenoliths in volcanic pipes (Upton et al. 1976). A variety of other metamorphic rocks also occur, which are different from the neighbouring Dalradian metamorphic rocks of the Highlands (Upton et al. 1983; 1984).

The Llanvirn-Ashgill sedimentary succession at Girvan, which covers the Ballantrae Complex, is considered by Bluck (1983) to be a proximal fore-arc deposit. This suggests that the Midland Valley is the site of an Ordovician arc, presumably on continental basement, which is no longer exposed. An alternative view, proposed by Yardley et al. (1982), Leggett (1980), and Leggett et al. (1983), is that the Midland Valley was a fore-arc basin in Ordovician and Silurian times. These views are discussed by Bluck (1985).

To the south of the Ballantrae Complex is the Southern Uplands, an Ordovician-Silurian accretionary complex (McKerrow et al. 1977; Eales 1979; Leggett et al. 1979; Leggett 1980; Leggett et al. 1982). This terrane represents sediments scraped off an oceanic plate subducting towards the north. Upton et al. (1983; 1984), on the basis of xenoliths in volcanic deposits, and Hall et al. (1983; 1984) on seismic grounds have shown that the Southern Uplands are probably underlain by a basement similar to that under the Midland Valley, which suggests that the Southern Uplands terrane is allochthonous, and has been thrust northwards over the Midland Valley (Bluck & Halliday 1982; Bluck 1983; Hall et al. 1983; Upton et al. 1983). The Southern Uplands are separated from the Midland Valley and the Ballantrae Complex by the Southern Uplands fault, a major tectonic boundary.

### 1.2.3 The Ballantrae Complex

The Ballantrae Complex (fig 1.2) covers approximately 80 km<sup>2</sup>. It is an ophiolitic complex composed predominantly of fault-bounded blocks of serpentinised ultramafic rocks, and basaltic lavas and volcanoclastic sediments, some of which are spilitised. As such the complex is an important piece of evidence for plate-tectonic interpretations of the British Caledonides. Balsillie (1932; 1937) has given a detailed description of the complex while Church & Gayer (1973) compared the Ballantrae Complex to Newfoundland ophiolites.

Radiometric and palaeontological dating of the Ballantrae Complex, summarised by Bluck (1985), shows that most of the complex was formed and assembled between 505 and 476 Ma, i.e. between the Tremadoc and the Llanvirn in the early Ordovician. The exception is a 576 Ma date for a garnet-clinopyroxenite block from a melange-olistostrome unit. This also contains blueschist fragments, and may represent the remains of an older ophiolitic terrane (Bluck 1985).

The Ballantrae Complex consists of a number of fault-bounded blocks running in a roughly SW-NE direction. There are two blocks of serpentinite, with blocks of spilitised basaltic lavas and volcanogenic sediments between, and to the north and south of the serpentinites. The final component of the complex is a gabbro-diorite-trondhjemite complex exposed on Byne Hill and Grey Hill (Bloxam 1968; 1981), in the north-east of the complex. Although Lewis & Bloxam (1977) attempted to construct a single stratigraphic section

for the lava blocks, geochemical studies have shown that they originated in different tectonic environments (Wilkinson & Cann 1974; Thirlwall & Bluck 1984), and have been structurally assembled in their present positions. There is also evidence from chromite compositions that the two serpentinites have separate origins (P. Stone pers. comm.), with the northern serpentinite originating in a sub-island arc position, while the southern serpentinite could have formed either beneath an island arc, or at a mid-ocean ridge.

Beneath the northern serpentinite belt there is a dynamothermal aureole (Spray & Williams 1980; Treloar et al. 1980), with layers of garnet-metapyroxenite, amphibolite and greenschist, representing the welding of successively shallower crustal rocks to the base of a rising slab of hot peridotite. Similar aureoles have been found in other ophiolitic terranes, e.g. the Bay Of Islands complex in Newfoundland (Spray 1984).

The various components of the Ballantrae Complex are typical constituents of ophiolite complexes, and the Ballantrae Complex is regarded as an ophiolite (Church & Gayer 1973; Dewey 1974), although it has no real sheeted dyke complex as found in other ophiolites.

It is generally accepted that ophiolites represent ancient oceanic crust, generated either at a mid-ocean ridge or in a back-arc basin. This implies that the Ballantrae Complex is the remnant of an Ordovician sea floor, but there is no general agreement as to whether it is the remnant of a marginal basin (Bluck et al. 1980), an ocean floor (Lambert & McKerrow 1976) or an ocean island (Barrett et al.

1982). The marginal basin hypothesis is favoured because the geochemistry of the lavas indicates that they formed in a variety of petrotectonic environments (Thirlwall & Bluck 1984), including island arc and intraplate settings, but there is very little material which appears to have been generated at a mid-ocean ridge. These environments could all be found close together in a marginal basin, and be brought together structurally during the closing of the basin. The presence of different petrotectonic environments within the complex suggests that the blocks were assembled tectonically, i.e. that the faults between blocks represent major discontinuities rather than just a late cutting up of a homogenous complex by relatively minor faults. Finally, it must be noted that the association of the Ballantrae complex with the remains of an ocean rests more on a comparison with similar ophiolitic rocks elsewhere than on internal evidence from the complex itself.

#### 1.2.4 The Pinbain Lava Block

The Pinbain lava sequence (fig 1.3) is a fault-bounded block within the Ballantrae Complex, composed of basaltic lavas and volcanoclastic rocks. Rushton et al. (1986) have assigned the block a lower Arenig age, on the basis of graptolite faunas from a thin shale unit at the base of the succession. Most of the lavas and volcanoclastic rocks have been spilitised, i.e. their plagioclase feldspars have been replaced by albite, resulting in the bulk chemistry becoming unusually sodic. The rocks have undergone a metamorphic event which has resulted in the growth of new mineral

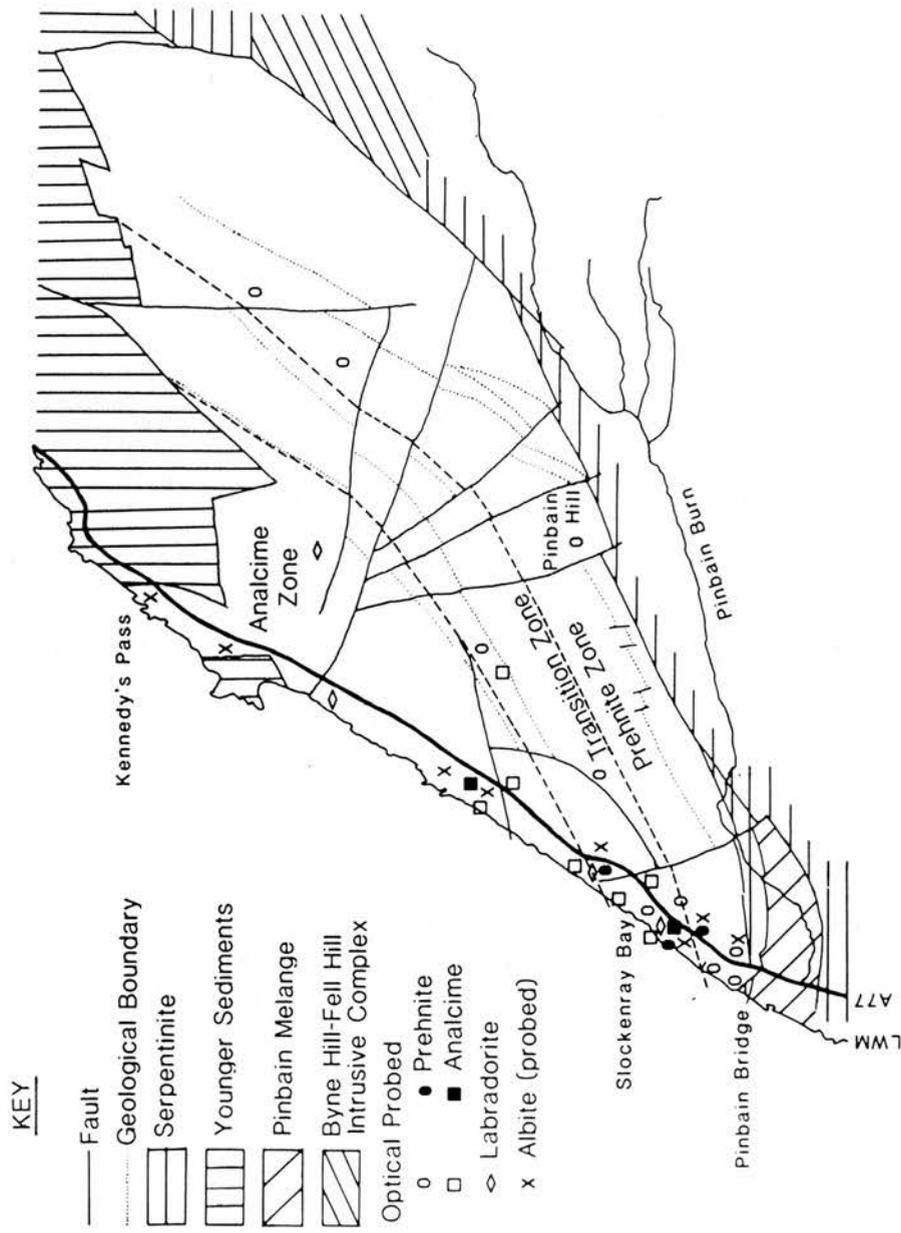


FIG 1.3. The Pinbain Lava Block. For explanation of metamorphic zoning see chapter 2.

phases such as chlorite, prehnite and analcime (Smellie 1984b), which are characteristic of very low grade metamorphism.

The Pinbain sequence is exposed along the coast from Kennedy's Pass [NX 2149 5931] to a point about 150 m north of Pinbain Bridge [NX 2137 5914] (fig 1.3). It extends about two kilometres inland, although exposure is poor except on the coast. The sequence is fault-bounded to the south and east against the northern serpentinite and the Byne Hill-Fell Hill intrusive complex. The throw of these faults cannot be estimated, since the pre-faulting position of the serpentinite and the Byne Hill-Fell Hill complex are unknown. The faults are, however, major features, and the fact that the various blocks are fault-bounded makes the reconstruction of stratigraphic or pre-faulting structural relationships very difficult.

To the north the lava sequence is unconformably succeeded by the Benan Conglomerate, the topmost unit of the Barr Group, and by the younger Ardmillan group sediments (Williams 1962), although the contact is often obscured by faulting and poor exposure. The Barr Group are the earliest sediments covering the Pinbain Block. The Balclatchie Formation, at the base of the Ardmillan Group, has a graptolite and conodont fauna indicating an early Carodocian age (Bergstrom 1971).

In general, bedding in the lava sequence strikes between north and north-east, and dips steeply north-westward. The stratigraphic thickness of the Pinbain Block is approximately 1 km, although there is much minor faulting, and the exact thickness cannot be measured.

The rocks are right-way-up, as can be determined from graded bedding and in a few places by the orientation of lava pillows. Although there are numerous minor faults cutting the area, only those bounding the sequence appear to have major displacements.

Some previous work on the metamorphism has been carried out (Smellie 1984b; Oliver et al. 1984). This work suggests that the southern part of the Pinbain Block contains prehnite-pumpellyite facies assemblages, with albite-chlorite-sphene as the typical mineral assemblage, while the northern part contains smectite, analcime, and a zeolite, with or without chlorite and sphene, and with remnant labradorite feldspar. This represents a zeolite facies assemblage. In addition, Bluck (1981) has suggested that spilitisation occurred shortly after the lavas were erupted, while they were still hot on the ocean floor. The evidence for this is a well-known locality, Slockenray Bay, where lava flows have been spilitised, but lava clasts in neighbouring sediments have escaped alteration.

#### 1.2.5 The Kilranny Conglomerate

The Kilranny Conglomerate unconformably overlies the Pinbain Block to the north, along the coastal section. The Kilranny conglomerate is part of the Ardmillan group of sediments (Williams 1962). Further inland, the Pinbain lavas are succeeded by older sediments, the Benan conglomerate of the Barr Group, showing that the onset of sedimentation on the Pinbain Block was diachronous. The lowest part of the Kilranny conglomerate, at Kennedy's Pass, was

sampled as part of this study.

The Kilranny Conglomerate is a polymict, coarse, clast-supported conglomerate. The clasts are from a number of different sources, and include ophiolitic debris, other metamorphic fragments, and a reddened granite which has no locally exposed equivalent. The conglomerate is believed to have been rapidly deposited on a deep-sea fan, and the clast imbrication indicates that it was derived from the north i.e. it was not eroded from the present outcrop of the ophiolite (Anderton et al. 1979). Williams (1962) has suggested that sedimentation was controlled by faulting, leading to rapid subsidence, and the accumulation of a thick sedimentary pile.

The Kilranny conglomerate was studied in order to determine whether the sedimentary cover has undergone the same metamorphic history as the Pinbain Lava Block. This information is important for the understanding of the timing of the metamorphism and the assembly of the Ballantrae Complex.

#### 1.2.6 The Pinbain Melange

The Pinbain melange has been described by Peach & Horne (1899) and by Bailey & McCallien (1952). It lies to the south of the Pinbain Lava Block, and is separated from it by a fault-bounded wedge of serpentinite. It is an olistostrome-type unit containing clasts of various rock types, set in a matrix of black silty shale. Peach & Horne (1899) reported that Arenig graptolites had been found in the

silty matrix, but Rushton et al. (1986) have cast doubt on the identification, and state that no age can be given for the melange. The majority of clasts are up to 1 m in diameter, and consist of lava, limestone, greywacke, amphibolite, dolerite, diorite, black shale and epidote schist. In addition, fragments of glaucophane schist have been found (Balsillie 1932). There are also some large blocks of basalt, tens of metres across, which may be large slide blocks in the melange.

Geochemical studies indicate that the lava clasts contained within the melange are from a different geo-tectonic environment than the Pinbain Lava Block (Thirlwall & Bluck 1984). The variety of rock types present in the melange units in the Ballantrae Complex suggest that they may represent an older ophiolitic terrane which formed the basement over which the Ballantrae Complex was emplaced (Bluck 1985).

The Pinbain melange was studied in order to compare its metamorphism with that of the Pinbain Lava Block. The degree to which these blocks share a common history will be an important piece of evidence for the structural and metamorphic history of the Ballantrae Complex, because if the metamorphism affects both blocks in the same way, then the Complex must have been assembled prior to the metamorphic event.

### 1.3 METHOD OF PRESENTATION

The three rock units, the Pinbain Lava Block, the Kilranny Conglomerate and the Pinbain Melange were studied using the same techniques, with the emphasis on identifying similarities and contrasts between them. To reflect this, this thesis is divided into chapters on the basis of the method of investigation, and the results for each unit will be presented either simultaneously, or as separate sections, as seems appropriate for each technique.

The techniques used can be divided into three categories. The first category uses petrography to identify metamorphic and original phases and their relationships (chapter 2), X-ray diffraction to determine the clay mineralogy (chapter 3), and the electron microprobe to identify, and measure the composition of the mineral phases (chapter 4). This information provides constraints for the temperature and physical conditions of metamorphism. Secondly, X-ray fluorescence was used to determine the bulk chemistry of the rocks, in order to compare it with unaltered basalts, while the trace element chemistry can be used to identify the tectonic environment in which they originated (chapter 5). Finally the nature of the fluids involved was investigated by determining the hydrogen and oxygen stable isotope ratios of the rocks (chapter 6), and by studying fluid inclusions within veins which presumably contain a sample of the original fluid (chapter 7).

When all this information is put together a more complete picture of the metamorphism, or alteration (for the purposes of this study these two terms are considered to be synonymous), can be built up. The temperature, the nature of the fluid, and the extent of chemical changes within the rock are all important for the understanding of the metamorphism. This can then be put together with other data in order to build up a better understanding of the nature of the Ballantrae Complex, and its position in the development of the Caledonides. This will be discussed in chapter 8, and final conclusions will be presented at the end of the thesis.

CHAPTER TWO

PETROGRAPHY

2.1 INTRODUCTION

The Pinbain lava sequence consists of volcanic and volcanogenic rocks, the original petrography of which has been overprinted by very low grade metamorphism. Because of this, the original igneous petrography must to some extent be inferred from the presently existing metamorphic petrography. The macroscopic petrography will be considered first, then the original igneous petrography. This will be followed by consideration of the metamorphic petrography and the petrography of the vein systems. These last two studies allow the definition of a system of metamorphic zones which will be discussed at the end of the chapter (section 2.8.3).

2.2 MACROSCOPIC FEATURES

The well-exposed sequence along the coast contains a variety of rock-types, generally volcanic or volcanogenic, with plagiophyric basalt being the most common rock (and clast) type. There are also some clinopyroxene-phyric basalts. The lavas are most common at the base of the succession, with more sedimentary material coming in higher in the sequence. 42% of the succession consists of lavas (Bluck 1981).

The lavas are usually present in massive flows, but some pillowed units also occur. Vesicles are present in many of the lavas, generally filled with calcite, although analcime and clay and/or chlorite also occur as vesicle fillings. Solid, massive, coarsely plagiophyric basalts (plagioclase up to 10 mm) occur to the north of Slockenray Bay, but elsewhere the lavas tend to be both brecciated and jointed, and these two features can occasionally be confused. Some of the brecciation occurs in in-situ lavas, having formed by autobrecciation during cooling. The "clasts" are homogenous, and can often be fitted together across cracks to reform pillows and flows. Some of the lavas have reddened flow tops, which Smellie (1984a) has interpreted as the result of subaerial weathering.

Some of the lavas have been reworked into sedimentary breccias, with non-matching clasts (which may themselves be derived from autobreccias). These breccias contain more matrix material than the autobreccias. There are some relatively texturally mature breccias with partly rounded clasts, and there are some sandstone units, often tuffaceous. The autobreccias, and breccias derived by local resedimentation of the autobreccias are highly angular, and clast supported, but there are also conglomerates with rounded clasts, particularly at Slockenray Bay. Some of these are matrix supported, and may be debris flows. Bluck (1981) has shown that these deposits form "hyalotuff deltas", and are locally derived from flows erupted at shallow depth and eroded by wave action. Smellie (1984a) has found accretionary lapilli in tuffaceous sandstone units, which shows that shallow submarine or subaerial volcanic activity occurred probably

within a few kilometres of the Pinbain Block. This evidence suggests that either there was generally shallow water in the area, or there were large volcanic edifices approaching sea level.

The rocks have in many cases retained their original macroscopic textures, i.e. their porphyritic character, and the auto-brecciated texture, but the very low grade metamorphism has caused changes in appearance. The greatest change is the general green appearance of the rocks, which is perhaps their most obvious feature. This colour is caused by the large amount of chlorite and clays in the rocks. The colour ranges from a greenish grey to a bright green, depending on the amount of chlorite and clays present. The brightest green colours are restricted to the surface of the rock, and are often associated with a crumbly texture which suggests that it is caused by recent weathering producing clays, rather than by the metamorphic chlorite. Not all the Pinbain rocks are green, however. Some have a red or purple colour, which is caused by the presence of iron oxides which, together with sphene and chlorite, makes up a great deal of the matrix of the rocks (see section 2.4).

Extensive veining is another prominent macroscopic feature of the Pinbain rocks, the sediments as well as the lavas. The veins range in size from being scarcely visible, up to vein complexes over 30 cm wide, in which there is more vein material than original rock. The most typical thickness is about 5 mm. The veins penetrate from one rock type to another, and are not restricted to single clasts. They are generally white in colour, and those that can be identified in hand specimen contain predominantly calcite. There are some veins

which have been stained red, probably by haematite.

An interesting feature in the Pinbain rocks is the presence of thin planes where the darker material appears to be concentrated. These resemble pressure-solution seams in limestone, and may have the same origin.

### 2.3 ORIGINAL MINERALOGY

Although the Pinbain rocks have been metamorphosed, much of the original petrography can still be discerned, either because minerals have escaped alteration or because they have been pseudomorphed by the metamorphic minerals. In addition there are some clasts of basalt in sediments from Slockenray Bay which have escaped the effects of the metamorphism.

#### 2.3.1 The Lavas

The original rocks were normal basic igneous rocks, containing plagioclase feldspar, clinopyroxene and opaque crystals, set in a very fine-grained or glassy matrix.

Plagioclase is the most common mineral phase. It occurs as rectangular phenocrysts up to 10 mm long, and also as lath-shaped microphenocrysts in the matrix, which are often flow-aligned. Plagioclase makes up varying amounts of the rock. Sometimes it is

completely absent. Other rocks contain only large phenocrysts, making up 10-30% of the rock, set in a non-crystalline matrix. When plagioclase phenocrysts and micro-phenocrysts both occur plagioclase can make up 70% of the rock. Plagioclase was probably crystallizing as the rocks were erupted, and the abundance of microphenocrysts is controlled by the length of time the rock remained in the magma chamber before eruption, and also by the cooling rate after eruption, with thicker flows continuing to crystallize plagioclase microphenocrysts until they solidify. Where plagioclase has escaped albitisation it can be identified as labradorite.

Some of the pyroxene in the Pinbain basalts shows a faint pinkish pleochroism which identifies it as titanaugite. It is present as small, usually roughly oval phenocrysts 2-3 mm long. It is generally quite heavily altered to chlorite, particularly along the edges of the grains. Clinopyroxene makes no more than 30% of the Pinbain basalts. It is present in some of the plagioclase bearing rocks, but there are also some lavas which have clinopyroxene as the main crystal-phase, with only subordinate plagioclase.

The original opaque phase in the Pinbain basalts has been largely destroyed during the metamorphic event. It was probably ilmenite, judging by the quantity of sphene which has grown in the matrix during metamorphism.

Much of the Pinbain lavas must have consisted originally of micro-crystalline material, or volcanic glass. None of this matrix has been preserved.

### 2.3.2 The Sediments

Most of the Pinbain sediments consist of breccias containing clasts of lava derived from within the succession. Microscopically the clasts show similar features to the lavas described above. However, there are also some sandstones within the succession. These contain mainly volcanic debris, including a large proportion of plagioclase crystals. There is also some quartz, and clasts of volcanic rock. The clasts are angular to sub-rounded, and the sandstones are poorly sorted, indicating that they are both compositionally and texturally immature, and presumably locally derived. The finer-grained material in the sandstones, and any original matrix and cement has not survived the metamorphism.

### 2.4 MINERALOGICAL CHANGES FROM NORMAL BASALT

The rocks of the Pinbain Block were originally normal basalts, and this section will discuss the changes which have occurred to produce the spilitised, very low grade metamorphic rocks now exposed. The original basalts were composed of labradorite feldspar,

clinopyroxene and volcanic glass. The original composition has been preserved in a few specimens which have escaped the pervasive alteration, but there has been extensive recrystallization, particularly of the matrix. The breccias are composed largely of fragments of lava which have been altered in the same manner as the massive lavas.

Clinopyroxene is found in various states of preservation. It can be almost fresh, but usually it is replaced to a considerable extent by chlorite and sometimes it is completely pseudomorphed by chlorite (plate 1). Some of the rocks appear to have pyroxene phenocrysts in hand specimen, which are difficult to see in thin section, having been completely replaced by chlorite and sphene. These pseudomorphs can be distinguished from the matrix because they have a lower proportion of sphene and iron oxides.

The plagioclase feldspars which are the main phenocrysts in the Pinbain lavas were originally labradorite, and some labradorite remains in the upper part of the succession. Most, however, has been replaced by albite, and some by potassium feldspar. Bluck (1981) has recorded blocks of lava from sediments in Slockenray Bay in which the feldspars have remained unalbitised. However, in other blocks from the same location the plagioclase has been replaced by albite. In one interesting example, the large phenocrysts have remained unalbitised, although there is a minor amount of replacement by potassium feldspar, while the small microlites from the same rock are albite. This suggests that albitisation may depend on the ease of fluid access as well as on temperature. The replacement has been incomplete in some



PLATE 1. Chlorite pseudomorphing 1 mm pyroxene crystals. S13.

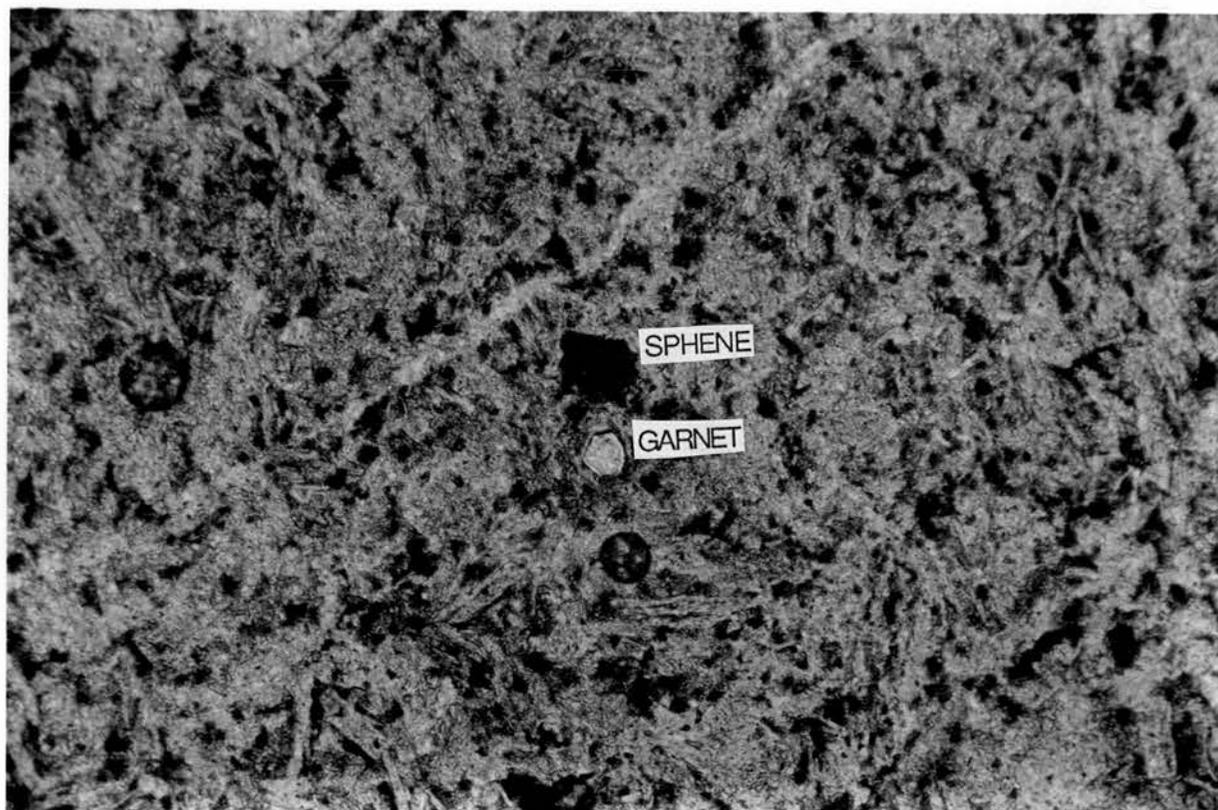


PLATE 2. Sphene (possibly pseudomorphing opaques) and garnet. The sphene is 0.1 mm across. P14A.

grains, and it can be seen that the boundary between albite and labradorite is irregular, with no evidence that the albite represents an original igneous zonation.

In addition to being albitised, the feldspars have been extensively altered, with the formation of sericite (plates 4 and 5). Other phases found replacing feldspar include analcime, chlorite, prehnite, clinozoisite, and in some cases calcite. These phases are frequently found in greater abundance near cracks in the feldspar, due to the easier transport of elements necessary for their growth. An interesting specimen has an albite vein which joins a phenocryst which has been albitised, with optical continuity across the grain boundary (plate 5). This indicates that the albitisation event was contemporaneous with the albite veins, which, as discussed below (section 2.5.2), belong to a single veining event.

It is not clear why some of the plagioclase grains should be highly altered, while others are almost fresh. There is no relationship between the degree of replacement by albite and the amount of other secondary minerals replacing the feldspar. Both albite and labradorite grains can be found which are almost completely unaltered. The answer is probably that the extent of alteration depends on the ease of fluid access. Since both albite and labradorite have been altered in this way, the sericitisation must have occurred during or after the albitisation.

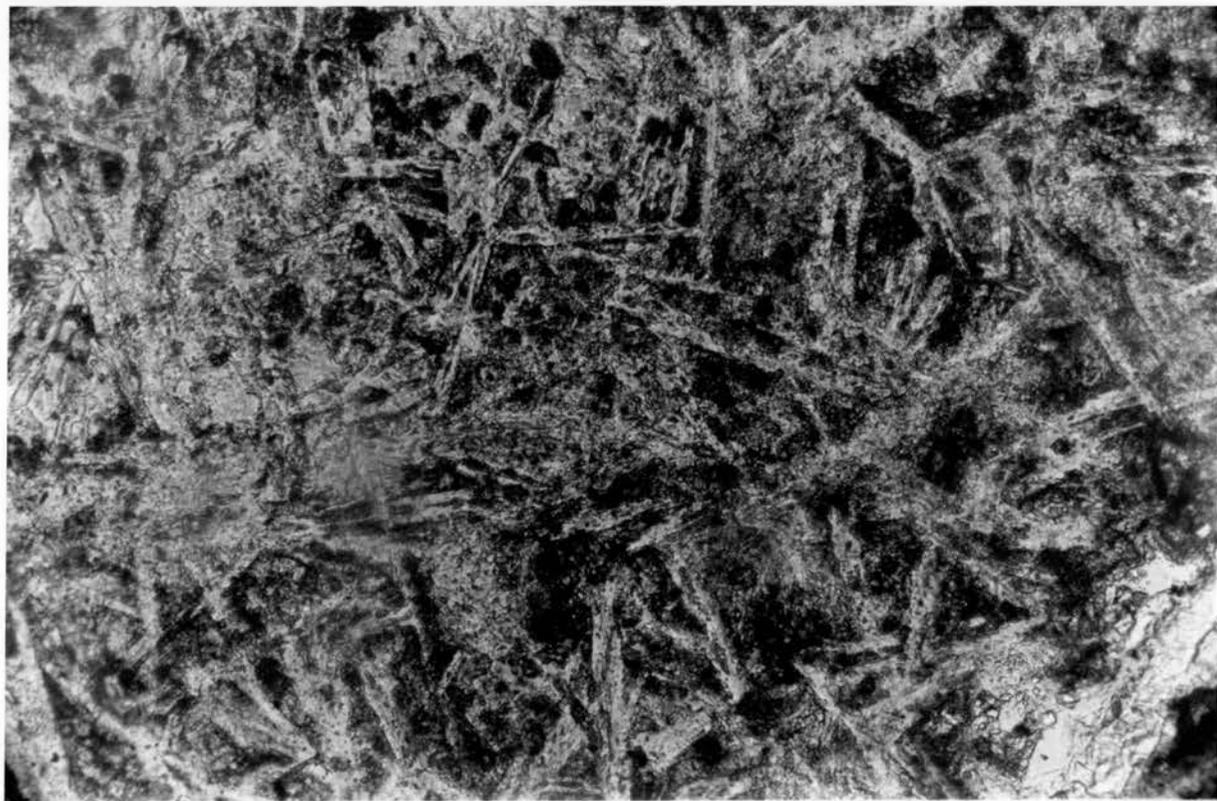


PLATE 3. Typical chlorite-albite-sphene matrix (0.1 mm albite crystals). P22

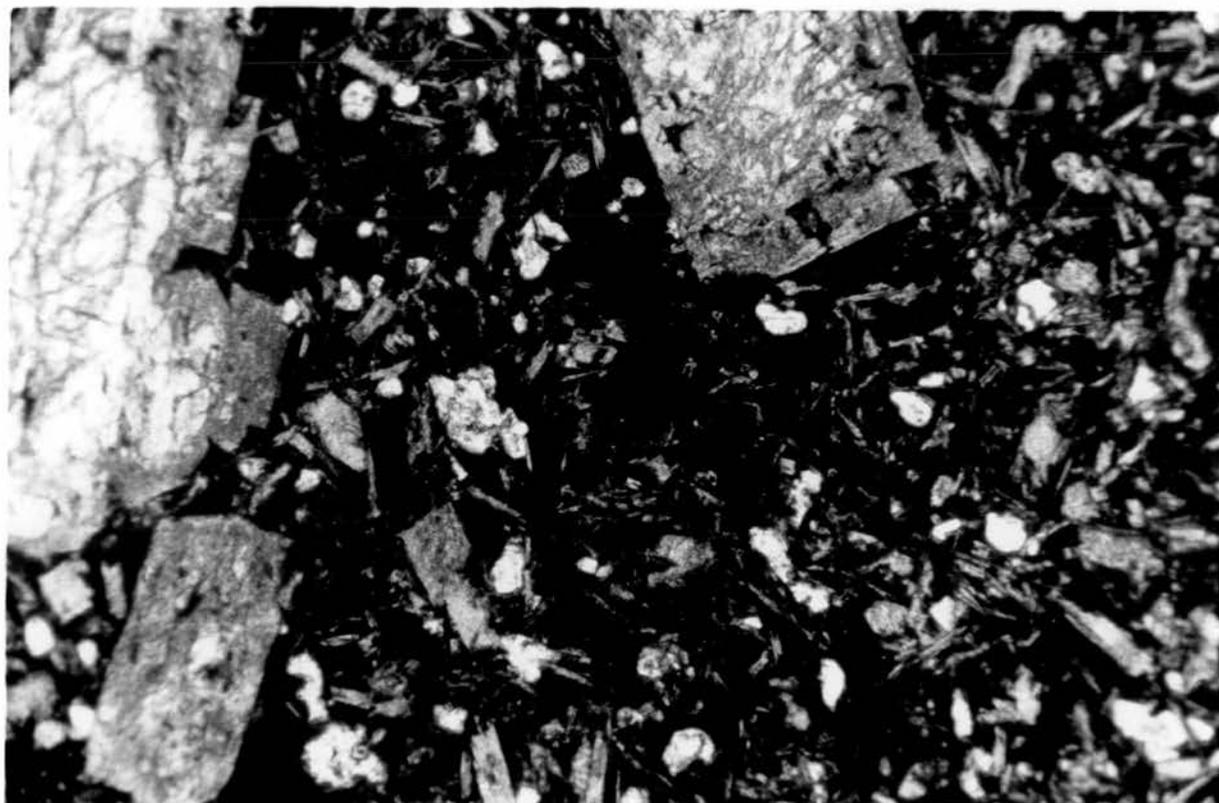


PLATE 4. Sericitized albite phenocrysts in iron-stained matrix. Phenocrysts 1 mm across. S4

The original glassy matrix of the Pinbain lavas has been replaced almost entirely by a brown, finely crystalline mixture of chlorite, sphene, and a brown material which is probably amorphous iron oxide (plates 3 and 4). The texture is spongy, with ragged grains of brownish chlorite, usually very small (about 20  $\mu\text{m}$ ), and oval sphenes, which stand out with high relief, and relatively high order interference colours which are usually partly masked by the dark brown colour of the sphene. Some larger sphene grains also occur, possibly replacements of original opaque minerals (plate 2). The fine-grained minerals are often so small, and so closely intermixed that it is difficult to identify them. There is much reddish-brown staining which is almost certainly caused by very fine grained iron oxides. This indicates that there must have been an oxidising environment during the alteration.

There are some minor constituents of the groundmass. At the base of the succession prehnite occurs within the matrix, and pumpellyite has been reported by Smellie (1984b). Garnets are occasionally found in the ground mass (plate 2). Calcite can be found as small grains near veins, which may have resulted from leakage of the vein fluid into the rock. At the edge of veins, and where small veins terminate, vein minerals are found intergrown with matrix minerals, indicating that the veining and the growth of metamorphic minerals in the matrix was contemporaneous.

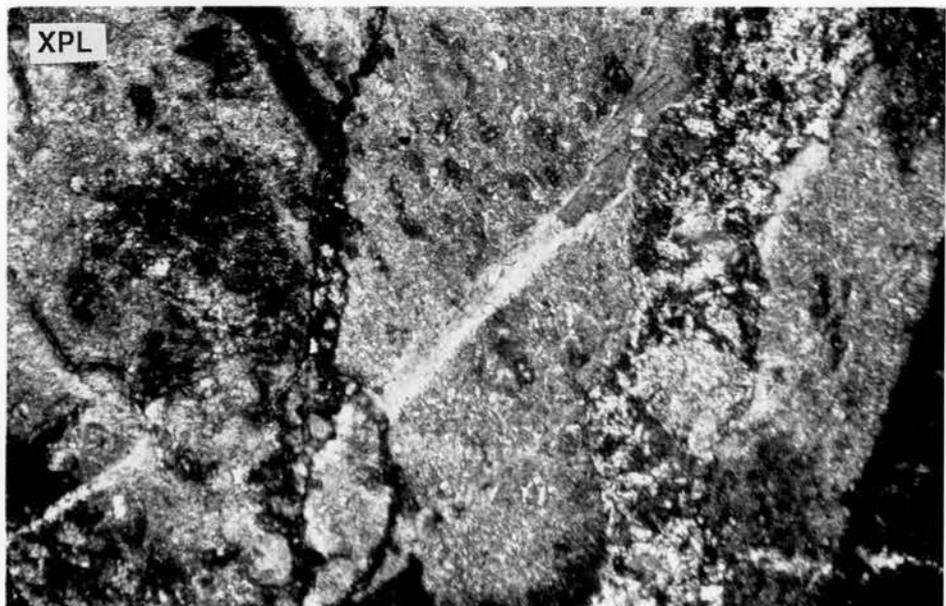
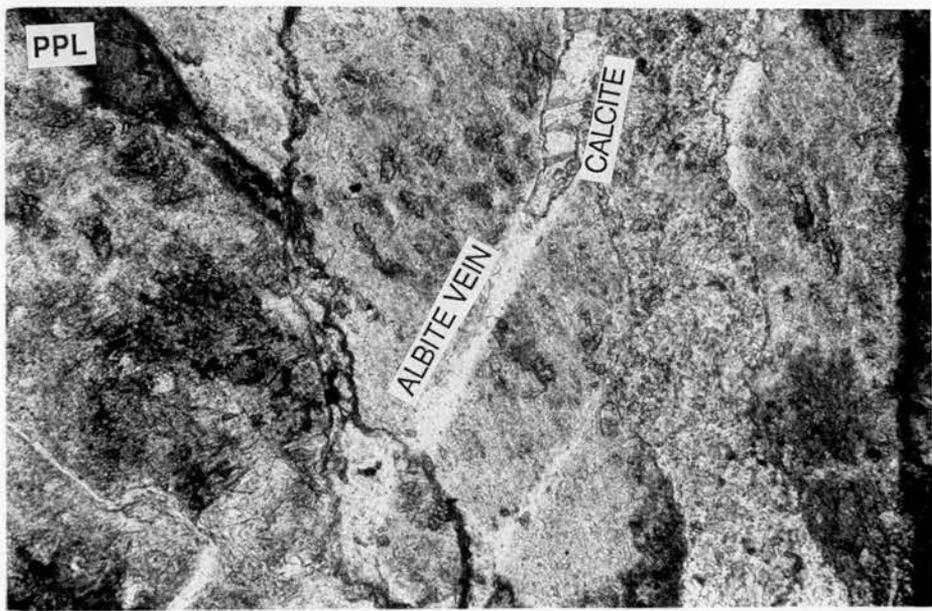


PLATE 5. Albite vein in optical continuity with 1 mm wide sericitised albite crystal. S7.

Clasts in the sediments are altered in much the same way as the lavas. The matrix of the sediments consists largely of chlorite, and chlorite can be seen growing across clast edges and into the matrix.

The characteristic matrix mineral assemblage throughout the Pinbain Lava Block is albite-chlorite-sphene, rather than the smectite + albite, chlorite, sphene suggested by Smellie (1984b). Where smectite does occur it is an additional phase, and may have been developed retrogressively. Prehnite and pumpellyite join the assemblage at the base of the section.

## 2.5 VEINS AND VESICLES

### 2.5.1 Vein and Vesicle Minerals

Calcite is the most common vein mineral. It can occur on its own, or associated with any of the other vein minerals. It has the usual calcite features of very high birefringence, "twinkling", and lamellar twinning. Grains of calcite are generally irregular, but have angular boundaries. Grain size is extremely variable, from a few  $\mu\text{m}$  up to 10 mm. The calcite frequently contains very large numbers of very small fluid inclusions, causing a clouded effect at low magnifications. The largest veins and vein complexes in the Pinbain Block contain predominantly calcite, with occasional quartz and calcite.

Quartz is the second most common vein mineral, being found in association with calcite, prehnite, analcime or chlorite, or in thin monomineralic veins. It occurs as irregular grains, generally with angular boundaries. In some cases the quartz has a feathery appearance, with indistinct sub-grains, and undulose extinction (plate 6). This is probably caused by rapid crystallization, rather than being a result of stress. Grain size varies from a few  $\mu\text{m}$  to about 2 mm.

Chlorite is also abundant as a vein and vesicle mineral. It occurs as a rim around most vesicles (plate 8), and also fills some. It has green-yellow pleochroism, and has low birefringence and moderately high relief. In some cases anomalous blue interference colours are seen. Chlorite occasionally seems to have unusually high birefringence, showing yellow colours, but this is due to body-masking, with the light green or yellow pleochroic colours obscuring the interference colour. Chlorite is generally fine grained, with the individual crystals rarely exceeding 200  $\mu\text{m}$  in length, but it often occurs in aggregates, sometimes fan-shaped or radial (plate 10). Chlorite occurs only with other minerals, mainly calcite and quartz.

Prehnite occurs in veins in the bottom third of the Pinbain succession. It has a characteristic blocky appearance with high relief and birefringence, and generally has a rectangular shape (plate 9). It occurs in patches in veins and vesicles associated with calcite, and it also forms some thin veins on its own. Prehnite grains vary in

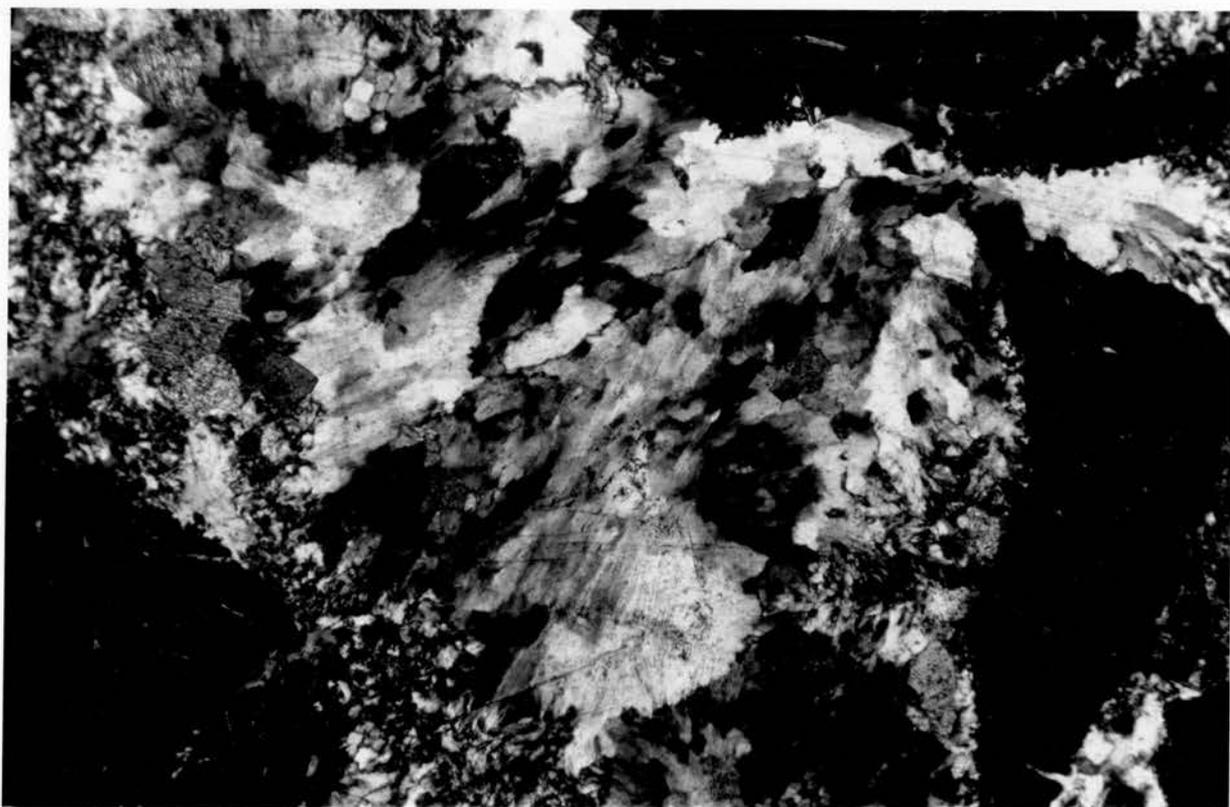


PLATE 6. Feathery quartz (field 3 mm wide). S19.

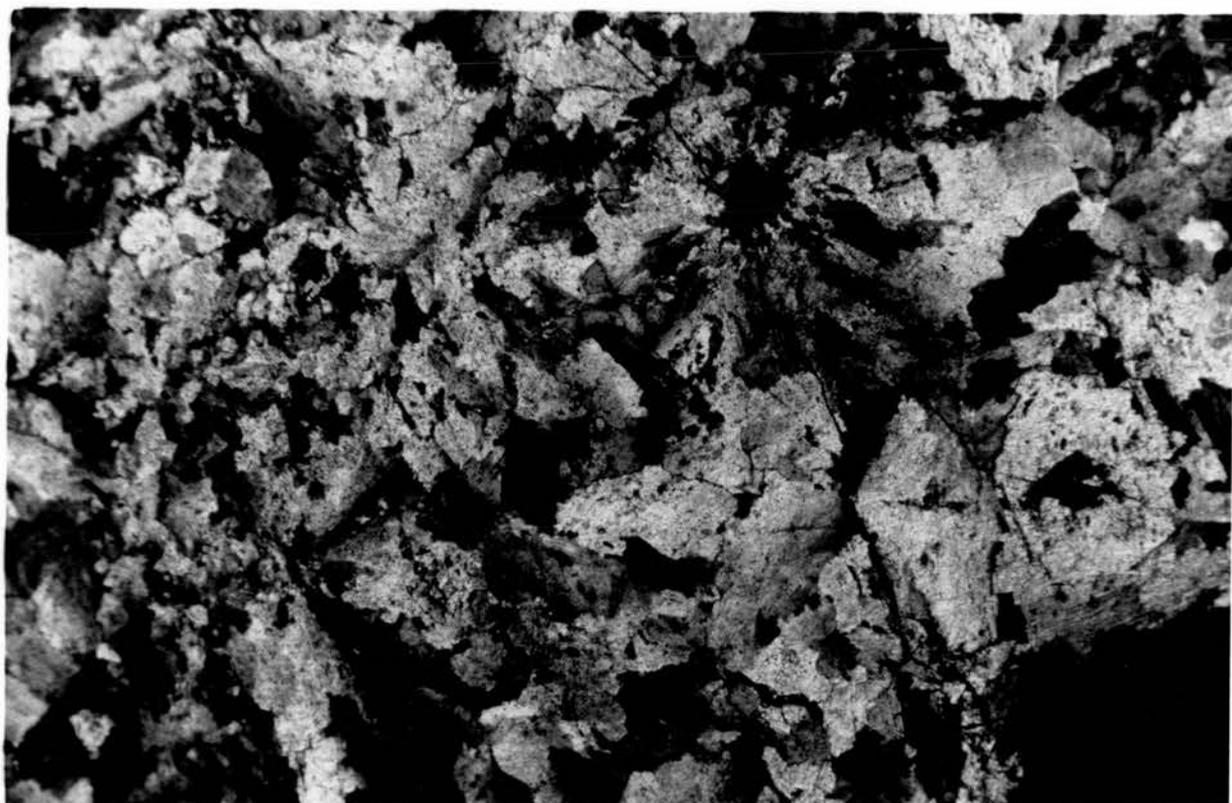


PLATE 7. Feathery prehnite (field 3 mm wide). S1A.

size from about 20  $\mu\text{m}$  up to about 500  $\mu\text{m}$ . Feathery, fan shaped prehnite grains occur in vesicles and some veins (plate 7). These show first order yellow birefringence colours, and are similar to some of the quartz grains, except that they have higher relief (compare plates 5 and 6).

Analcime occurs in the top two thirds of the Pinbain Block, generally above the zone in which prehnite occurs, although these zones do overlap. It has low relief, and although it has a cubic structure, in these rocks it shows a slight birefringence. It tends to occupy cavities, such as vesicles, in the rock, and its form is governed by the shape of the cavity (plate 8). Cavities containing analcime are frequently rimmed by chlorite (plate 8), probably because of interaction between the fluid and the surrounding rock. Analcime does not grow until the layer of chlorite isolates the fluid from the bulk of the rock. Some analcime occurs in thin veins, associated with quartz and calcite. Single grains vary in size with the size of the cavity, with vein analcime being as small as 10  $\mu\text{m}$ , while vesicle grains can be 2 or more mm. In fine veins the analcime grains follow the vein morphology, and are long and thin.

Other minerals occur in veins in small amounts: albite is found in thin (<1 mm) veins (plate 5), as is potassium feldspar. These minerals occur as long, thin grains which follow the morphology of the veins they occur in.

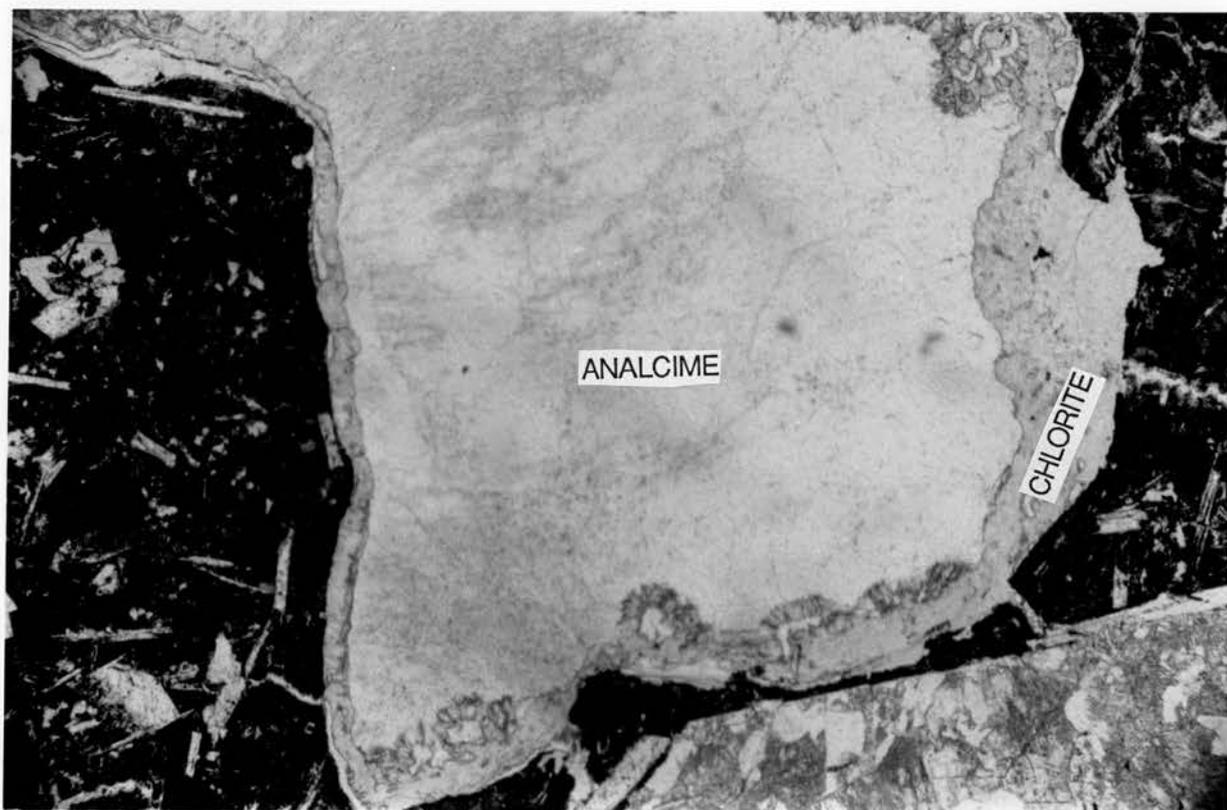


PLATE 8. 2 mm wide analcime amygdale with chlorite lining. P26.

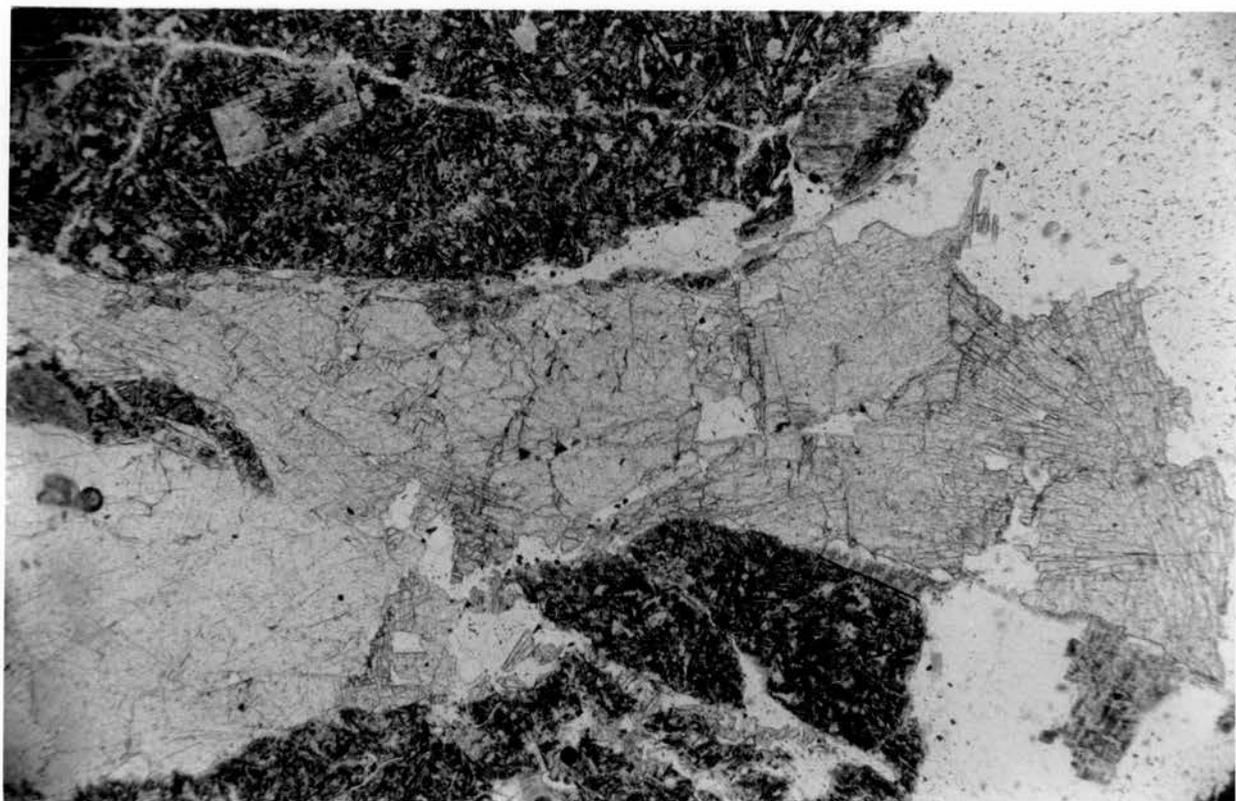


PLATE 9. 1 mm wide prehnite vein. P22.

Garnet has been found in a few veins and vesicles in the lower half of the succession. The garnet occurs as small (0.1 mm), grey, hexagonal or rectangular grains, with very high relief. In many cases they show a faint grey birefringence, rather than being completely isotropic.

Sphene is commonly present in small amounts in veins in the Pinbain section, occurring as small (0.1 mm) oval, dark brown grains. The birefringence of the sphene is frequently masked by its colour. Some patches of sphene may represent fragments of the original rock which have been "cut off" by veins.

#### 2.5.2 Vein and Vesicle Types

The vein minerals are present throughout the succession, with the exception of analcime and prehnite, which are restricted to their zones (section 2.8.3). The occurrence of the other minerals does not seem to be related to depth in the succession, being present in more or less equal amounts throughout. There is no consistent temporal relationship between different kinds of vein, i.e. everything can be found crosscutting everything else. Pure calcite veins are the most common type, with calcite-chlorite next, while calcite-chlorite-quartz and calcite-quartz are less common. Many veins show changes in mineralogy along their length, with patches of minerals being restricted to parts of the vein.

The veins can be divided into two types. Group 1 veins are the largest, and most extensive veins. They are relatively simple in mineralogy, containing mainly calcite with some quartz, chlorite and with occasional prehnite at the base of the section. It was from these veins that fluid inclusion wafers were prepared (chapter 7).

The other group of veins, group 2, contain a wider variety of minerals, including analcime, prehnite and albite, along with the ubiquitous calcite, chlorite and quartz. These veins are smaller than the major veins, no larger than 1 cm, and often as small as 10  $\mu\text{m}$ . The veins are frequently so thin that they are occupied by single crystals succeeding each other along the length of the vein. The larger veins in this group can contain combinations of two or three of the minerals, but prehnite and analcime are not found in the same veins, although they do occur within the area of a single thin section.

The vesicles are generally filled by calcite, but fillings of calcite and chlorite, analcime, prehnite and occasionally clays are found. Analcime vesicles never contain calcite.



PLATE 10. Radial chlorite aggregates in calcite amygdale (field 3 mm wide). XPL. P16

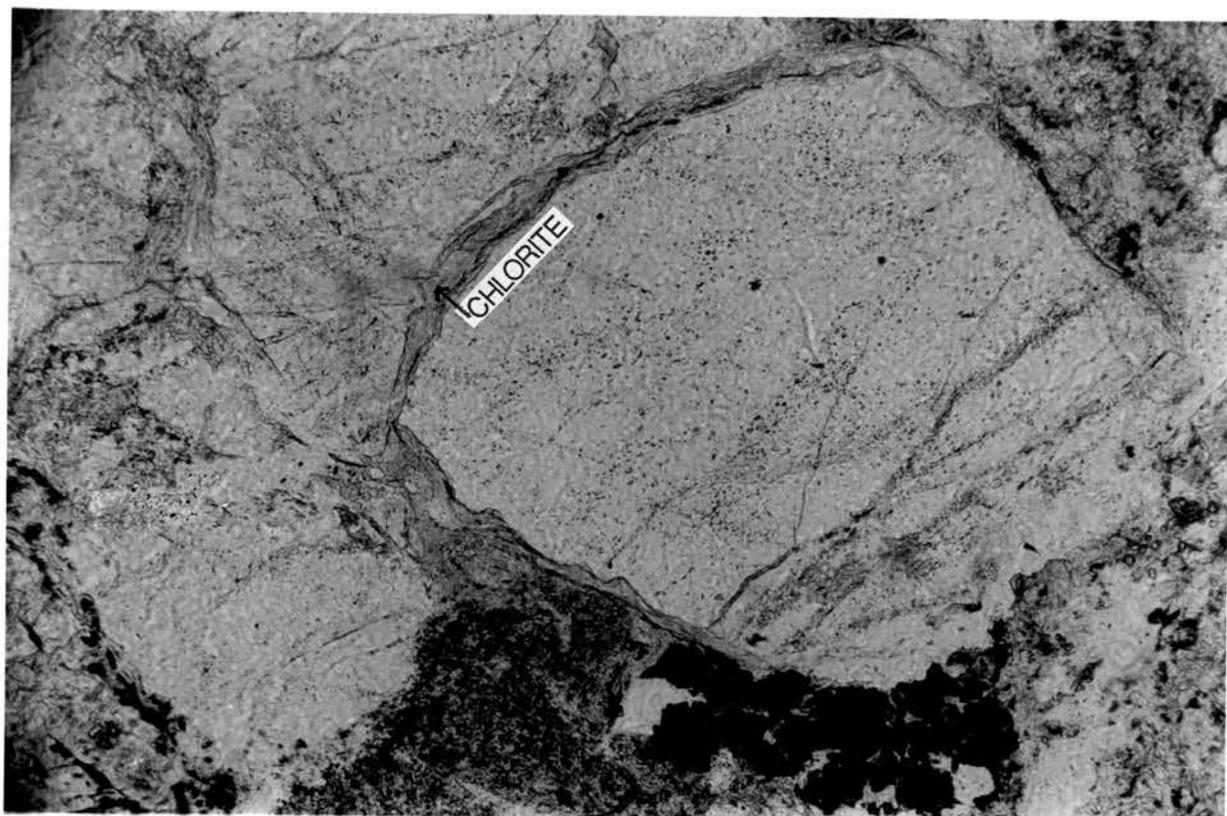


PLATE 11. Chlorite overgrowing and veining a 0.5 mm wide albite clast. P39A.

## 2.6 THE PINBAIN MELANGE

The Pinbain Melange is a chaotic sedimentary assemblage of clasts ranging in size from small pebbles to large blocks tens of metres in diameter, embedded in a fine-grained, silty matrix. The matrix is volcanogenic. The clasts are of varied provenance, being predominantly altered basalt, but there are also clasts of volcanogenic sandstone, limestone, and metamorphic rocks, including small fragments of blueschist and eclogite (Balsillie 1932). With the exception of the limestone all these lithologies can be found in situ in other parts of the Ballantrae Complex. Although this is a sedimentary melange (olistostrome), there is also evidence of shearing in the fine-grained matrix. The Pinbain Melange probably represents debris eroded off an advancing ophiolitic nappe, with large blocks sliding off the nappe into the finer-grained sediments. The shearing within the matrix may have been soft-sediment deformation due to the large slide-blocks, or it may be the result of the ophiolite nappe riding over its own debris. This would help to account for the chaotic nature of the melange. It is quite probable that both mechanisms operated to produce the shearing.

The lava clasts and blocks in the Pinbain Melange have undergone essentially the same changes as the prehnite zone of the Pinbain lava sequence. The occurrence of pumpellyite (Smellie 1984b) and prehnite suggests that the metamorphic grade is approximately the same as the base of the Pinbain Block. The melange has a matrix of fine-grained, shaly sediment, which contains considerable amounts of chlorite.

The most interesting feature of the lava breccias in the melange is that they show evidence for two generations of veining. The first, in which veins of calcite were formed, occurred before the lavas were eroded because the veins are cut by the edges of clasts. The second generation of veining occurred after the formation of the melange, because the veins can be seen to cut through both the clasts and the matrix of the melange. This generation of veining contains prehnite, as well as calcite and quartz.

Some of the metamorphism of the lava clasts in the melange might have occurred before the formation of the melange, but the vein prehnite, and the chlorite growing in the sedimentary matrix of the melange shows that the melange has also been metamorphosed after assembly.

## 2.7 THE KILRANNY CONGLOMERATE

The Kilranny Conglomerate is part of the cover of the Ballantrae Complex and lies unconformably on it (Williams 1962), although the contact is frequently disturbed by faulting. It is a coarse (10 cm) grained clast-supported polymict conglomerate. The main clast type is a granite with pink-stained feldspars which is not exposed locally (Williams 1962). Other clasts which are found include spilitised basalts, and other ophiolitic debris similar to the rock types now exposed in the Ballantrae Complex, but since the Kilranny Conglomerate has sedimentary structures indicating derivation from the north

(Williams 1962), it is unlikely that the clasts were derived from the Ballantrae Complex as now exposed. In the late Ordovician ophiolitic rock-types must have covered a greater area than they do at present. The matrix of the conglomerate is relatively fine grained, with silt and clay grade material which is greenish in colour. The conglomerate is penetrated by calcite veins which pass through both the matrix and the clasts.

It is not possible to say whether the spilite clasts in the conglomerate were altered before the conglomerate was formed, or whether, as in the breccias in the Pinbain Block, the spilitisation occurred after deposition. There has been some alteration since deposition, however, because veins of calcite and chlorite can be seen cutting across clast boundaries, and the edges of clasts are often overgrown by chlorite (plate 11). Quartz veins also occur. This mode of alteration is similar to that seen within the Pinbain Block, and this suggests that the metamorphism occurred after the deposition of the Kilranny Conglomerate, and was possibly due to the burial of the sequence under the sedimentary cover. It may be argued that the alteration of the Kilranny Conglomerate is merely diagenetic, but it is so similar to that of the Pinbain Block that the distinction does not seem very meaningful, i.e. diagenesis is transitional to burial metamorphism with increasing depth.

## 2.8 DISCUSSION AND CONCLUSIONS

### 2.8.1 The Relationship Between Veins, Vesicles and the Rock

Veins in metamorphic rocks do not necessarily form at the same time, or under the same conditions as the metamorphic rock itself. In the Pinbain Block, fluid inclusion studies (chapter 7) indicate that the group 1 veins, the large veins with restricted compositions, formed from higher temperature fluids than the bulk of the rock. However, the smaller group 2 veins probably formed under similar conditions to the bulk of the rock. There are several lines of evidence that indicate this. Firstly, the veins contain minerals which occur in the bulk of the rock, such as prehnite, chlorite and albite. Secondly, at the ends of veins the vein minerals become intergrown with the rock minerals, with no evidence for reaction relationships. Thirdly, some of the veins are so small that it would be very difficult for fluid passing through to maintain a different temperature from the bulk of the rock, unless there were very high flow rates.

Analcime is different from the other minerals in that it only occurs in veins and in vesicles, and as a replacement of plagioclase, never as a matrix mineral. Analcime in the group 2 veins formed as part of the same event in which the other group 2 vein minerals grew, and therefore, like them, formed at the temperature of the bulk of the rock. The analcime in the vesicles occurs in the same rocks in which

analcime veins are found, and is therefore probably from the same event. This means that the occurrence of analcime can be used to understand the metamorphism of the rock (see below). The analcime occurs only in cavities or as a replacement of plagioclase. This is probably because analcime requires favourable chemical conditions in which to grow, which do not occur in the rock matrix. In analcime vesicles the first filling is a layer of chlorite, which probably serves to isolate the fluid from the chemical environment of the rock itself.

#### 2.8.2 Timing of albitisation

Bluck (1981) suggested that spilitisation, i.e. the albitisation of the plagioclase in the Pinbain lavas, occurred on the sea floor as a result of interaction between sea water and lava flows which retained their heat. Clasts eroded from the flows cooled too quickly to be affected. This theory is unlikely for several reasons. Firstly, spilitisation has not been observed to be a sea floor phenomenon in modern basalts. Most basalts dredged from the sea floor are fresh, or have suffered only some palagonitisation (Cann 1969). Where spilitites occur, they have been brought to the surface by faulting. Secondly, many of the clasts in sediments from Slockenray Bay and elsewhere in the succession are spilitised. Sometimes the small plagioclase crystals are albitised but the large ones are not, suggesting that possibly fluid access is the controlling factor. Thirdly, most of the lavas in the Pinbain Block are highly brecciated, with a large porosity. This would allow fluid access for

spilitisation, but it would also mean that the lavas would cool very rapidly, reducing the time available for spilitisation to take place. It would also reduce the chance that residual heat in the lava pile as a whole could account for the spilitisation of some of the sediments.

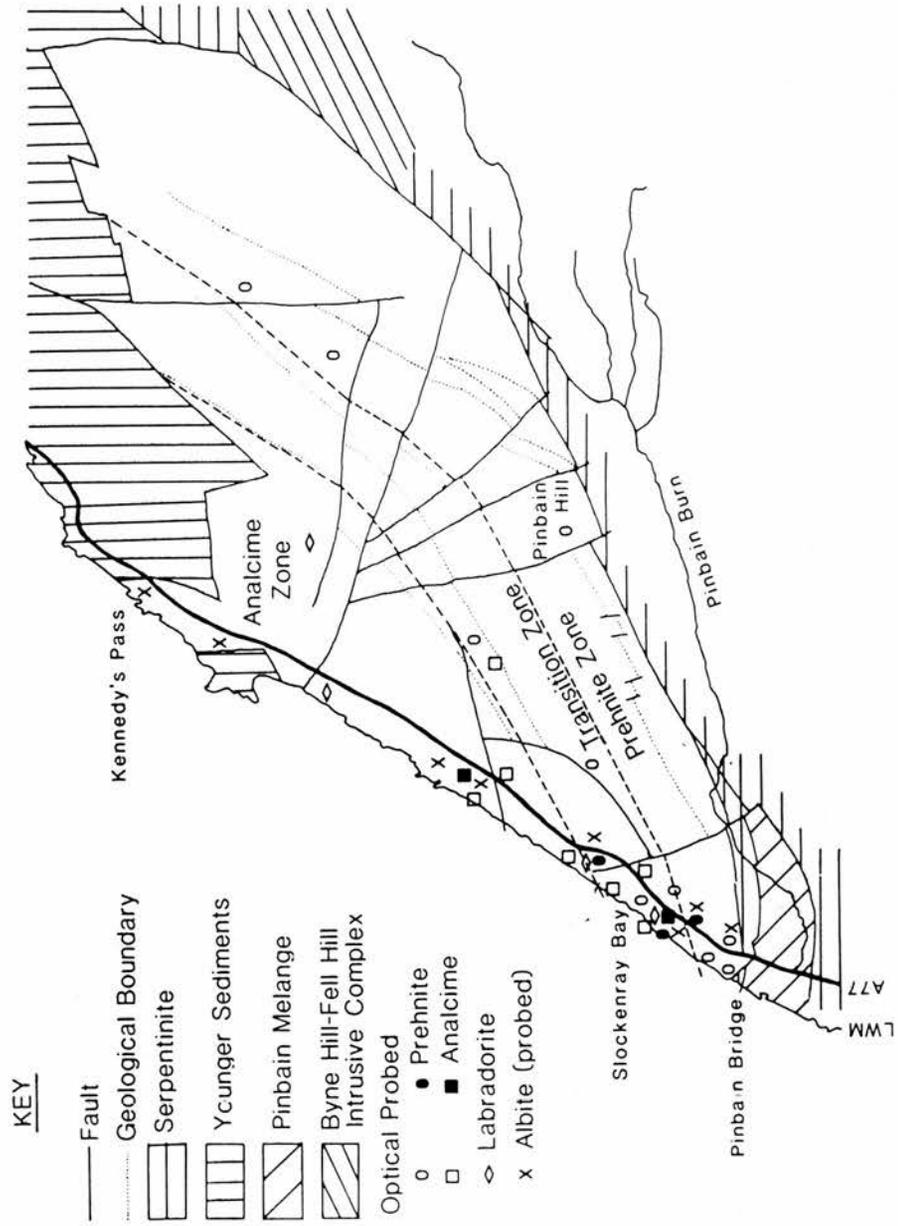
There is direct evidence that the albitisation of the plagioclase occurred at the same time as the veining, which, as shown in the previous section, occurred at the same time as the metamorphism of the rock. In one sample, an albite vein passes into an albitised phenocryst, with optical continuity, showing that the vein and the albite of the phenocryst formed simultaneously (plate 5).

Spilitisation is often a feature of burial metamorphism (Coombs 1974). The spilitisation of the Pinbain lavas was almost certainly a burial metamorphic change, since unaltered labradorite is only found towards the top of the lava succession. The rocks at the base of the succession must have been too hot to escape spilitisation, and in a pile containing a large proportion of sediment, the temperature difference must have been caused by burial. If spilitisation was dependant only on retained heat within a lava flow, there is no reason why unspilitised clasts and flows should not occur down to the base of the succession.

### 2.8.3 Metamorphic Zones

The metamorphic event established metamorphic zones in the section, which are approximately parallel to the strike of the rocks. In the southern, stratigraphically lower part of the section prehnite and occasionally pumpellyite occur. In the upper two thirds of the block analcime occurs as a vesicle filling, as a component of small veins, and as a replacement of plagioclase. The Pinbain Block can be divided into three zones based on the occurrence of these minerals (fig 2.1). The prehnite zone at the base is succeeded by the transition zone, where both analcime and prehnite occur, and the transition zone passes up into the analcime zone. Although inland exposure is poor these zones appear to run more or less parallel to the strike of the rocks. Veins within the Pinbain Melange contain prehnite, suggesting that the melange was in the prehnite zone, at the same level as the base of the Pinbain Lava Block when the metamorphism occurred. The alteration of the Kilranny Conglomerate probably occurred under the same conditions as the top of the analcime zone.

The occurrence of pumpellyite in the prehnite zone (Smellie 1984b) shows that the lowest part of the Pinbain Lava Block contains a prehnite-pumpellyite facies mineral assemblage (Coombs 1960, 1961). The analcime zone is in the zeolite facies (Coombs et al. 1959).



**FIG 2.1.1.** Metamorphic zones in the Pinbain lava block. (Map based on BGS 1:10,000 sheets NX19 SW & SE, resurveyed 1979-83 by J. L. Smellie & M. J. Gallagher).

#### 2.8.4 Temperature Of Metamorphism

The boundary between the prehnite zone and the transition zone is marked by the appearance of analcime, which occurs together with quartz. Analcime and quartz become unstable together, and react to form albite and water, in a reaction which has been investigated by Campbell & Fyfe (1965), and then by Liou (1971a). Campbell & Fyfe concluded that analcime and quartz become unstable at a temperature of 190 C, and at lower temperatures at higher pressures. Liou's experiments showed that analcime and quartz break down to form albite with intermediate structure at about 200 C, but that since in nature low albite is formed the equilibrium line for the reaction is slightly less than this, at about 190 C, or lower at higher pressures. These data show that the boundary between the transition zone and the prehnite zone must represent a metamorphic temperature of 190 C or less.

Prehnite can be stable at temperatures as low as 90-130 C (Boles & Coombs 1977), and it is stable up to a temperature of 400 C (Liou 1971b). The coexistence of analcime and prehnite in the transition zone is thus feasible, although it is not often reported. Richter & Roy (1974) found coexisting analcime and prehnite in volcanic rocks from Maine, USA.

CHAPTER THREE

CLAY MINERALOGY

3.1 INTRODUCTION

X-ray diffraction techniques have been used to identify the fine-grained clay minerals present in all the samples from the Pinbain Block, and in the lava clasts from the Pinbain melange. The results are similar, and are presented together.

3.2 METHOD

X-ray diffractograms were prepared at St. Andrews University, using a Philips PW1010/PW1349 X-ray diffractometer. The diffractometer was run from 3 to 35° at one degree per minute. The measured 2-theta angles were converted to d-spacings, with reference to the position of the quartz 3.34Å peak as a correction for machine drift.

The 2-6 µm fraction of powdered rock was separated by centrifuging, mixed with water into a slurry, and then allowed to settle onto a glass slide. This method of preparation allows the platy clay minerals to become parallel to the slide as they settle, which is useful because clay minerals are identified by variations in (001) reflections. The degree of orientation is, however, reduced by the presence of particles of hydrated iron oxides, which are

unfortunately very common in the Pinbain rocks. This means that the basal reflections are less well defined than they could be.

The non-phyllsilicate minerals in the samples were identified using the JCPDS (1974) powder diffraction data for minerals, and search manual, while the methods outlined by Thorez (1976) were used to identify the clay minerals and chlorite.

### 3.3 RESULTS

Untreated samples gave a peak for approximately 7 Å with a secondary peak at approximately 14.5 Å which dominate the diffractogram. Other peaks which were significant in some samples were the strong quartz peak at 3.34 Å and the albite peak at about 3.2 Å. A low, broad, poorly defined peak at about 10 Å is probably due to the presence of poorly crystalline illite or white mica. This material was probably formed by the alteration of feldspar, and the poor definition of the peaks may be due to the presence of slight variations of the composition of the mineral depending on its local chemical environment, as well as to poor crystallinity.

Fig 3.1a shows diagrammatically the low angle part of a typical diffractogram. The 14.5 Å peak indicates the presence of chlorite and/or smectite. The presence of chlorite is confirmed by the presence of the 7 Å peak, as well as by examination of thin sections. Most published diffraction data shows that the intensity ratio between chlorite 14.5 Å and 7 Å peaks is around 100:70. However, in the

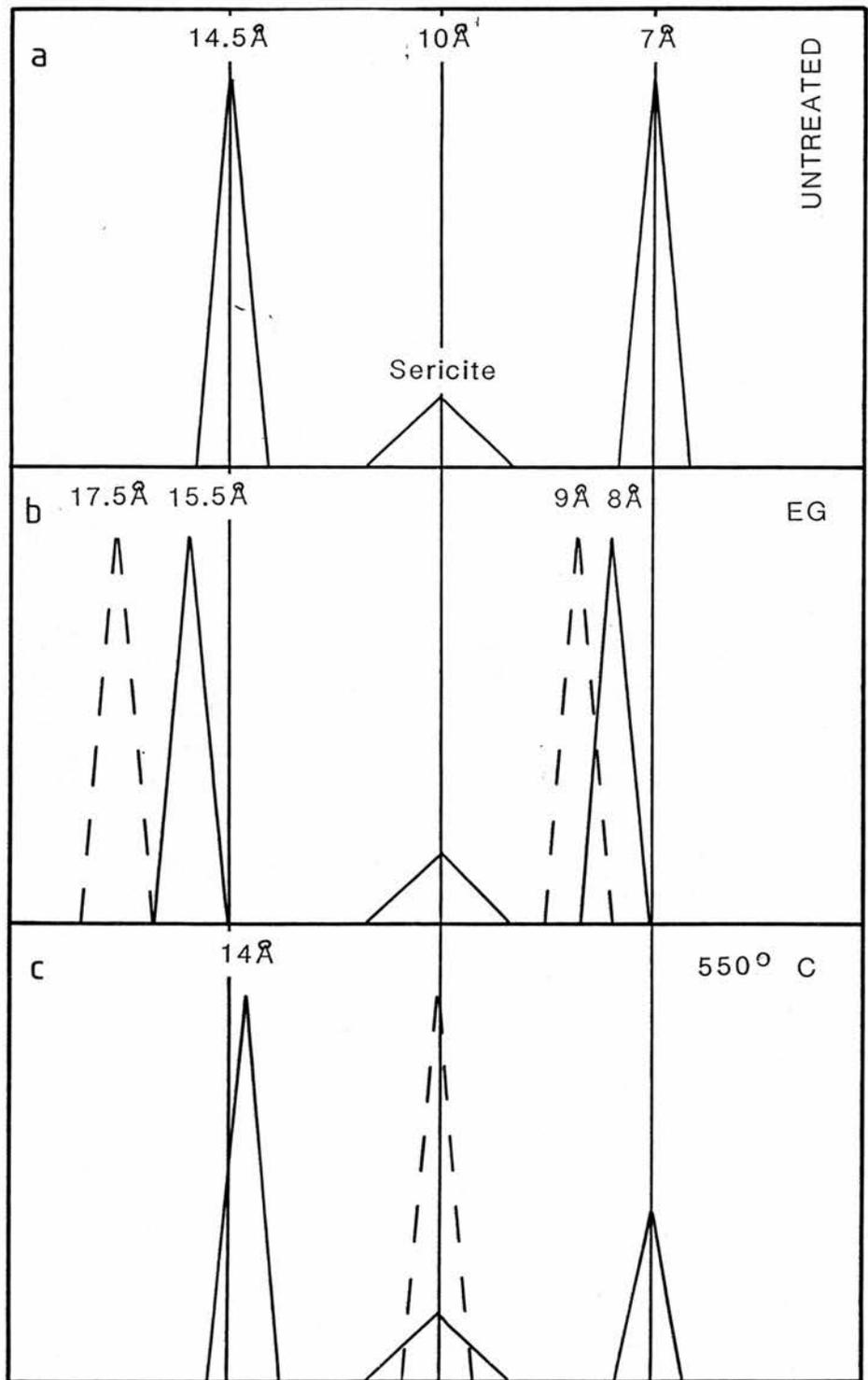


FIG 3.1. Diagram of XRD results from the Pinbain Block. Broken lines show expected smectite behaviour.

Pinbain samples the ratio tends to be smaller, often around 100:100. This suggests that smectite may be present, masked by the chlorite peaks. To confirm this various treatments were used.

In the first treatment, glycolation, the sedimented chips were placed over a bath of warm ethylene glycol. The glycol is absorbed by smectite and resulting in an expansion of the basal reflection from 14.5 Å to 17.5 Å. Normally chlorite will not be affected. In the samples from Pinbain, however, there is an expansion, but it is only to about 15.5 Å (fig 3.1b).

When heated to 550<sup>o</sup> C the 14.5 Å peak of smectite collapses to 10 Å while chlorite shows only a small reduction in its basal spacing and the intensity of its 002 reflection at about 7 Å is reduced. The Pinbain samples generally show chlorite behaviour (fig 3.1c). However, small amounts of smectite may be present, because their collapsed 10 Å peaks may be lost in the broad humps already present at 10 Å.

#### 3.4 CONCLUSIONS

These results indicate that the chlorite is a variety known as swelling chlorite, which absorbs ethylene glycol because of degradation of the brucite layers of the chlorite structure (Thorez 1976). This suggests that the chlorite has suffered from some alteration since its formation. The presence of a small amount of smectite inter-layers cannot be ruled out, however, because they would

give a slightly more expanded peak which will be lost in the high angle background and in the broad base of the expanded chlorite peak.

One sample from the transition zone definitely contained smectite, with little or no chlorite. The behaviour of smectite is shown in comparison to chlorite in fig 3.1. Smellie (1984b) has recorded smectite from the Pinbain rock, and it has also been identified using the electron microprobe (G. Oliver pers. comm.), but the XRD results suggest that it is not generally an important component of the Pinbain rocks. It is probably present throughout the sequence in small quantities. Smectite is frequently found as a low-temperature weathering product of basalts (Deer et al. 1980), and with the evidence of degradation of the chlorite, i.e. its swelling character, it seems likely that the smectite was produced by lower temperature alteration as the sequence cooled after the peak of the metamorphism. Any smectite produced before the peak of the metamorphism would probably have reacted to form chlorite as the temperature increased.

The Pinbain melange lavas have the same clay mineralogy as the Pinbain Block, which suggests that they may have been metamorphosed under similar conditions.

CHAPTER FOUR  
MINERAL CHEMISTRY

4.1 INTRODUCTION

Mineral chemistry was investigated using a JEOL electron microprobe at St. Andrews University. The purpose of the electron microprobe investigation was twofold: firstly to confirm the optical identification of mineral phases, which was often extremely difficult because of the fine grain size, poor crystal form and general "messiness" of the altered basalts; and secondly to investigate the possibility of changes in mineral composition with depth in the succession. This second investigation was carried out on the ubiquitous chlorite and feldspar.

The petrography of the mineral phases is described in detail in chapter 2, and will not be considered here.

4.2 RELICT MINERALS

The Pinbain spilites, along with those from the melange, have had their original igneous textures preserved to a large extent, and some of the original igneous minerals, mainly pyroxene and occasionally plagioclase, have also survived the very low grade metamorphism. Both plagioclase and pyroxene were examined using the electron microprobe,

and the results of this study are discussed in this section. Plagioclase is also discussed in the metamorphic minerals section, below, because it has commonly been replaced by albite.

#### 4.2.1 Pyroxene

Clinopyroxene has been optically identified throughout the Pinbain lava block and the melange (chapter 2), and the pyroxene from the lava block was studied using the electron microprobe. The analyses of pyroxene were made in order to compare the pyroxene chemistry with other pyroxenes found within the Ballantrae Complex. This is possible because the pyroxenes are occasionally well-preserved, and there is a good chance that the original chemistry has been preserved. The bulk chemistry cannot be used for this purpose because there has been metasomatism (chapter 5). The analyses are given below :-

Oxide	S4	S4	S4	S14	S14	P26
SiO <sub>2</sub>	44.49	46.49	46.32	51.59	50.97	51.19
TiO <sub>2</sub>	3.45	3.02	3.64	1.04	1.04	1.54
Al <sub>2</sub> O <sub>3</sub>	6.65	5.89	6.13	2.57	2.68	3.88
FeO	11.75	12.51	11.98	8.53	8.00	7.67
MgO	10.37	11.91	11.63	15.77	15.57	15.27
CaO	20.50	20.64	20.20	20.33	20.33	20.70
Na <sub>2</sub> O	0.65	0.53	0.48	0.27	0.21	0.19

The consistency of results from within each sample suggests that the pyroxenes have not had their compositions significantly altered, because if they had been altered by fluids during low grade metamorphism it would be highly unlikely that each grain would be altered to the same extent. Pyroxene is unstable at low temperatures, and in contrast to feldspars no new pyroxene can form as a replacement of the old one.

The table shows that the pyroxenes from S4 are extremely high in titanium and aluminium and can be classified as aluminium-rich titanaugites (Deer et al. 1980), as they show the characteristic violet-purple pleochroism. The other samples are augites, but they also contain a high proportion of titanium and aluminium.

These pyroxenes are very similar in composition to those described by Holub et al. (1984) which came from a suite of basaltic dykes found cutting the metamorphic sole beneath the northern serpentinite (Treloar et al. 1980). If the Pinbain lavas are derived from the same magma as the dykes then the Pinbain Block must postdate the obduction of the peridotite slab. This conclusion is supported by comparison of the trace element geochemistry (Chapter 5).

#### 4.2.2 Plagioclase

The plagioclase from the Pinbain rocks has in most cases been replaced by albite, but three probe analyses were made of relict plagioclase in phenocrysts. The full analyses are given in appendix 1.1. The analyses correspond to molecules containing 51.2, 62.9 and 57.9% anorthite respectively. These can be classified as labradorite (Deer et al. 1980). The remainder of the molecule is albite, except for one sample, S4, which contains 7.9% of the orthoclase molecule and 31.8% of albite. This analysis is from a plagioclase phenocryst which is partially altered to potassium feldspar, and the high orthoclase content probably represents incipient alteration rather than an original feature since it is rare for plagioclase to contain more than 5% of potassium feldspar (Deer et al. 1980). Labradorite feldspar is a typical constituent of basic igneous rocks, and the identification of labradorite relics, altering to albite in places is evidence that the spilites were originally basalts.

#### 4.3 METAMORPHIC MINERALS

The most common metamorphic mineral phases were examined using the electron microprobe. Some rare minerals were not located in the polished thin sections, e.g. epidote, and it proved impossible to obtain analyses of possible clay minerals because they could not be polished.

#### 4.3.1 Feldspar

Electron microprobe investigations have confirmed the pervasive nature of the albitisation in the Pinbain Block. As shown in fig 4.1, out of 35 feldspar analyses in 9 rocks, 24 had anorthite contents of less than 10%. Of the rest, four analyses, two of which were from veins, had >95% K-feldspar, and two more vein feldspars had K-feldspar contents of 75% and 62% respectively. Two feldspars had oligoclase compositions, and there were only three examples of labradorite. Electron microprobe results have shown that the potassium feldspar in phenocrysts is replacing labradorite. The 35 analyses are given in full in appendix 1.1.

Cho et al. (1986) have examined a contact metamorphic sequence in the Karmutsen metabasites of Vancouver Island, British Columbia, and have discovered that the albite in the zeolite facies rocks has approximately 3-4% anorthite in general, with a range of even higher values in some samples. In contrast to this, albite in the prehnite-pumpellyite facies rocks has only 1-2% anorthite. This feature can be seen to some extent in the Pinbain rocks, because although the range of compositions in the analcime zone (zeolite facies) and the prehnite zone (prehnite-pumpellyite facies) is similar, the majority of the prehnite zone albites have more restricted compositions of around 1% anorthite (fig 4.1).

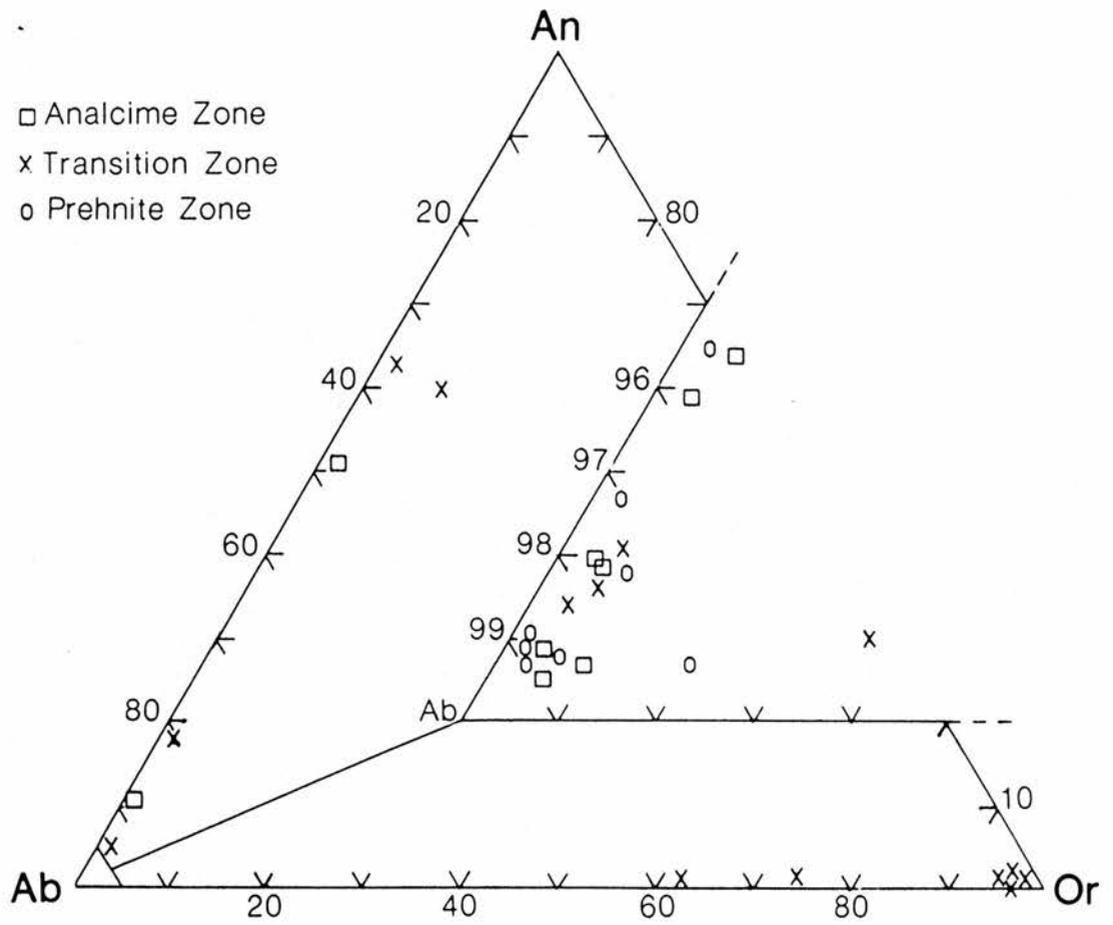


FIG 4.1. Feldspar compositions from the Pinbain Block.

#### 4.3.2 Chlorite

Chlorite has also been examined by electron microprobe. The full analyses are given in appendix 1.2. The results are plotted in fig 4.2, in the composition diagram used by Hey (1954). The chlorites have no compositional peculiarities, with a range from Si 5.55, Fe 7.1 to Si 7.75, Fe 2.8. The results define a distinct band of compositions, within which a change in composition with depth can be discerned. Chlorites from the prehnite zone generally have a higher ratio of iron to magnesium and are poorer in silicon than those from the analcime zone. The decrease in silica is balanced by an increase of aluminium in the tetrahedral sites (section 4.3.2.1), resulting in a charge imbalance which is probably compensated for by the introduction of aluminium and/or ferric iron into the octohedral sites usually occupied by ferrous iron and magnesium. This trend is similar to that discovered by L. Evans (pers. comm.) in the Clyde plateau lavas, and by Kuniyoshi & Liou (1976a) in a contact metamorphic aureole in the Karmutsen volcanics of Vancouver Island, British Columbia. In sequences with a relatively uniform chemical composition the chlorite composition can thus be used as an indication of grade, but caution must be exercised because other factors, such as the composition of the parent rock, and of the fluid phase can play a part (Kuniyoshi & Liou 1976b). However, the temperature control on chlorite composition appears to be the major factor within the Pinbain Block.

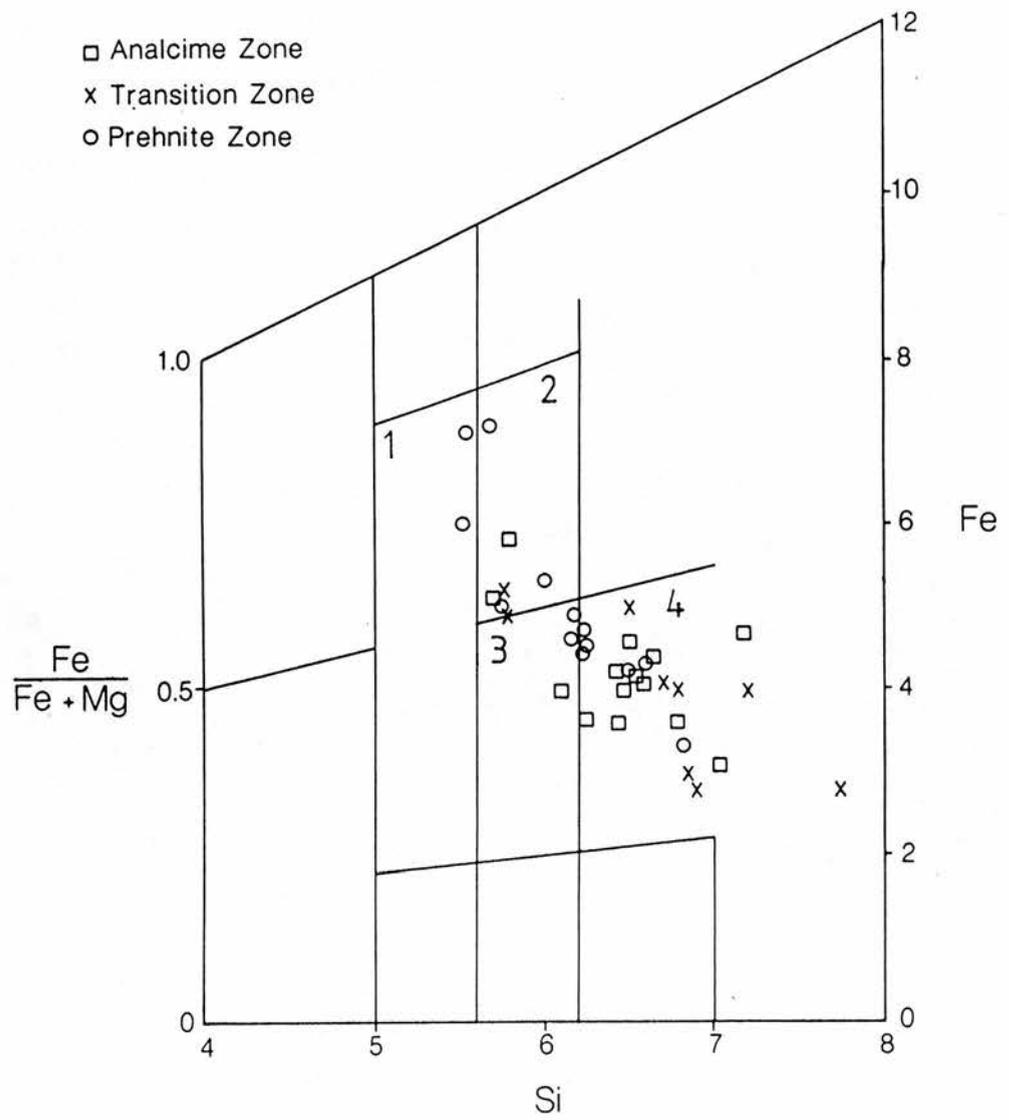


FIG 4.2. Chlorite compositions from the Pinbain Block.  
 1 = Ripidolite 2 = Brunsvigite 3 = Pycnochlorite  
 4 = Diabantite (Diagram after Hey 1954).

Chlorites from within the transition zone show rather more variation than those from elsewhere, and this may be due to the fact that metamorphic fluids in the transition zone would vary in composition depending on which of the possible mineral assemblages was crystallizing. In addition, the southern end of the transition zone seems to have contained a conduit for relatively hot water from deeper in the crust, and there may have been locally raised temperatures causing changes in chlorite composition.

#### 4.3.2.1 The Chlorite Geothermometer

Cathelineau & Nieva (1985) have shown that the amount of aluminium in tetrahedral sites in chlorites is dependant on the temperature. They give a line of temperature against tetrahedral aluminium (fig 4.3a), based on chlorites sampled from a borehole in a hydrothermal area, where the temperature is well-constrained. This method has been applied to chlorites from the Pinbain Lava Block. The results are shown in fig 4.3b. These results show that the prehnite zone chlorites have an average temperature of about 215 C, those from the transition zone give temperatures of 170 C, while the analcime zone chlorites have an average of 180 C, slightly higher than the transition zone.

These results compare quite well with the temperatures estimated using other methods, i.e.  $150-170\text{ }^{\circ}\text{C}$  from stable isotope considerations (chapter 6), and  $<190\text{ }^{\circ}\text{C}$  for the analcime-out isograd (chapter 2). The results from chlorites with different modes of occurrence, such as those replacing pyroxene, and those in the matrix overlap with each other. This implies firstly, that the amount of tetrahedral aluminium in chlorites is dependant only on temperature, and not on the local chemical environment, and secondly, that all the chlorite formed at the same temperature, and therefore presumably at the same time. This shows that there was only one phase of metamorphism.

There is a wide range of variation within each sample, and within each zone. This means that temperatures estimated using the chlorite geothermometer can only be considered approximate. However, even a rough estimate of temperature can be useful. In the results for Pinbain, there is certainly evidence that the prehnite zone was the hottest part of the succession, and that the chlorites probably grew at temperatures of between  $150$  and  $230\text{ }^{\circ}\text{C}$ .

### 4.3.3 Analcime

The analcime from the analcime and transition zones has a very simple and uniform chemistry. The average of seven probe analyses is given below :-

SiO <sub>2</sub>	55.74%
Al <sub>2</sub> O <sub>3</sub>	22.53%
Na <sub>2</sub> O	11.64%
<u>TOTAL</u>	<u>89.91%</u>

The 10% unaccounted for is water and no other elements are present in significant amounts. Full analyses are given in appendix 1.3.

No examples of grade dependant variations in analcime chemistry in metamorphic terranes have been reported, although Deer et al. (1980) do state that igneous analcimes show an increasing degree of substitution of sodium and aluminium for silicon at lower temperatures. However, they also stress that the mineral generally has an extremely uniform chemistry. The chemistry of analcimes from the Pinbain Block is very similar to that from other very low grade metamorphic sequences.

#### 4.3.4 Prehnite

Four prehnite analyses were made. They show considerable variation in the iron:aluminium ratio, but the analyses are all typical examples of prehnite. The analyses are given below.

<u>Oxide%</u>					<u>Average</u>
SiO <sub>2</sub>	42.58	43.33	42.82	42.74	42.87
Al <sub>2</sub> O <sub>3</sub>	18.86	20.65	21.95	23.53	21.26
FeO	6.97	4.88	3.01	1.72	4.14
CaO	25.69	26.15	26.74	25.64	26.05
-----					
TOTAL	94.61	95.35	94.89	94.03	94.32
-----					

These analyses are from samples which occur within a 200 m band in the transition and prehnite zones, so there is unlikely to be any significant variation in temperature between the samples. Surdam (1973), and Kuniyoshi and Liou (1976a) suggested that iron rich prehnite was more stable at high temperatures in a contact metamorphosed sequence of basalts in Vancouver Island, British Columbia, but Cho et al (1986) examined the same sequence and could not find any temperature dependant compositional variation. They found that there were large variations between grains in the same rock, and even within the same grain. This large variation in compositions crystallizing at the same temperature is similar to that found within the Pinbain Block, and presumably reflects variations in

fluid composition within the vein systems in which the prehnite crystallizes.

#### 4.3.5 Sphene

Four sphene analyses were taken. This is too few to discern any trends with depth, although there is some variation in composition from one sample to another. The average composition is given below :-

SiO	33.01%
<sup>2</sup>	
TiO	28.12%
<sup>2</sup>	
Al O	5.56%
<sup>2 3</sup>	
FeO	3.32%
<u>CaO</u>	<u>23.32%</u>
<u>TOTAL</u>	<u>93.33%</u>

The remainder is water. Full analyses are given in appendix 1.4.

This sphene is rich in aluminium, which can substitute for titanium in the sphene structure. No temperature-dependant compositional variations have been reported for sphene in metamorphic rocks.

#### 4.3.6 Garnet

Only one garnet analysis was made :-

SiO	38.24%
<sup>2</sup> Al O	14.38%
<sup>2 3</sup> FeO	12.57%
<u>CaO</u>	<u>34.37%</u>
<u>TOTAL</u>	<u>99.56%</u>

This analysis corresponds to a molecule composed of 67.5% grossular and 32.5% andradite. This is interesting because the only previous record of garnet in Ballantrae lavas is of hydrogrossular (Bloxam 1964). It is not significant in terms of temperature, however, because garnets can be stable down to about 100°C (Winkler 1979).

#### 4.4 DISCUSSION

##### 4.4.1 Relict Minerals

The examination of relict minerals allows us to make some deductions about the origin of the Pinbain Block, and thus the Ballantrae Complex as a whole. The presence of unaltered labradorite in these rocks identifies them as previously normal basalts which have undergone the process known as spilitisation, i.e. the replacement of the labradorite by albite, accompanied by the development of secondary

minerals such as chlorite and sphene in the groundmass. The identification of spilitisation as a secondary process at Ballantrae was first made by Balsillie (1937). Labradorite can usually be identified optically (chapter 2) in the Pinbain rocks, but in other spilites use of the electron microprobe may be useful in identifying small relics of labradorite within albite crystals which might otherwise be missed.

The clinopyroxenes in the Pinbain section are quite distinctive in composition, and their chemistry compares closely to that of pyroxenes found within dykes which cut the metamorphic sole at the base of the northern serpentinite (Holub et al. 1984). The metamorphic sole is believed to have formed during the obduction of the hot peridotite slab (Spray & Williams 1980), prior to its emplacement on the fore-arc and subsequent serpentinisation. The dykes were intruded into cold peridotite, as shown by their chilled margins, and before the serpentinisation, because they suffered some rodingitisation during this latter event (Holub et al. 1984). It thus appears that the Pinbain lavas were erupted directly onto the fore-arc.

#### 4.4.2 Metamorphic Minerals

Apart from the chlorite geothermometer (section 4.3.2.1), which gives temperatures of formation for chlorites, the examination of the metamorphic minerals has identified two factors which may potentially be used as relative grade indicators. These are 1), the iron content of chlorite, and 2), the anorthite content of albite. Of these, the albite composition will probably be more comparable between different areas, because it is caused by a disequilibrium within the grain (Cho et al. 1986), this being related directly to temperature because the metastability is caused by slow diffusion and reaction rates at low temperatures. Thus the degree of disequilibrium should be similar in different areas which have undergone similar burial histories. The chlorite composition however, depends on the chemistry of the rock and of the metamorphic fluids as well as the temperature (Kuniyoshi & Liou 1976b) and so it will not be directly comparable between sections, especially since it is not generally possible to determine the composition of the fluid phase during metamorphism.

The variability of chlorite compositions means that the iron content of a single chlorite cannot be correlated with a given temperature, but the fact that chlorite compositions in general have distinct trends with temperature may be useful for determining the structure of a section. Breaks in a compositional trend would indicate faulting, whereas repetitions of sections of the trend would show the presence of thrusts or folds. This technique could best be applied to sections containing rocks of uniform composition, e.g. sequences of basalt. Local changes in compositional trends could show

the presence of otherwise unseen intrusions by defining a thermal aureole.

CHAPTER FIVE

BULK CHEMISTRY

5.1 INTRODUCTION

The bulk chemistry of 23 samples from the Pinbain lava block was obtained by means of X-ray fluorescence, as described below. The major elements were recalculated to anhydrous values, to ensure comparability. The full analyses are given in appendix 2. Results were obtained for major, and a selection of trace elements. The analyses were used for two purposes, firstly the usually immobile trace elements were used to identify the petrotectonic environment in which the Pinbain rocks were formed (section 5.2), and secondly the elements, major and trace, were examined in order to determine their mobility under the conditions prevailing in the Pinbain Block during alteration (section 5.3).

5.1.1 Sample Preparation

Samples for chemical analysis were chosen on the basis of lithology and freedom from recent weathering. The acceptable lithologies were basaltic lavas, autobreccias which were derived from single lava flows and which contained a minimum of matrix material, and lava clasts from sedimentary breccias. The lithology is given in

the table of analyses (appendix 2).

Samples were prepared for analysis by having those areas which had obviously suffered from recent weathering removed with a grinding wheel. Areas which were heavily veined or contained abundant vesicles were also discarded, to prevent the analysis from being contaminated by the vein filling. In most cases, however, there were abundant small veins which were impossible to remove. The samples were then split using a Lake and Elliot hydraulic splitter with stainless steel jaws, and crushed in a jaw crusher to produce small chips. These were then ground in a Tema swing mill with tungsten carbide discs until less than 200 mesh size.

#### 5.1.2 Method/Equipment

The chemical analyses were obtained by X-ray fluorescence in the geology department of St. Andrews University, under the supervision of Dr. W. E. Stephens, and with the technical assistance of Mr. A. Calder. A Philips PW1212 X-ray fluorescence spectrometer was used, with a Rh tube for primary excitation. The major elements were determined from a fused glass bead prepared from 0.5g of rock powder and 2.5g of spectroflux 105 and ammonium nitrate as oxidant. The trace elements were determined from pressed powder discs prepared by pressing to 5 tons rock powder mixed with moviol as binder. The method and conditions are similar to those described by Norrish & Chappell (1977). Major elements were determined by reference to a monitor, H12, supplied by K. Norrish. Iron is expressed as total

Fe O<sub>2</sub>, and the weight loss of the rock sample on fusion is used as an estimate of loss on ignition. All calculations are performed by an on-line microcomputer.

The precision of the equipment, along with a comparison of measured against "accepted" values for a set of standards, giving an estimate of accuracy, are given in tables in appendix 2.

## 5.2 IMMOBILE TRACE ELEMENT GEOCHEMISTRY

The trace elements of altered basalts can be divided into two groups, those considered to be essentially immobile during alteration, such as zirconium, titanium, niobium, yttrium and the rare earths (e.g. Pearce & Cann 1973; Floyd & Winchester 1978) and those which are generally mobile, such as strontium, barium and rubidium. The immobile elements can be used to investigate the original lava chemistry, and in particular can be used to characterise the petrotectonic environment (Pearce & Cann 1973). The mobile elements are not useful for this purpose, but investigation of them may help to define the chemical and physical processes occurring during alteration.

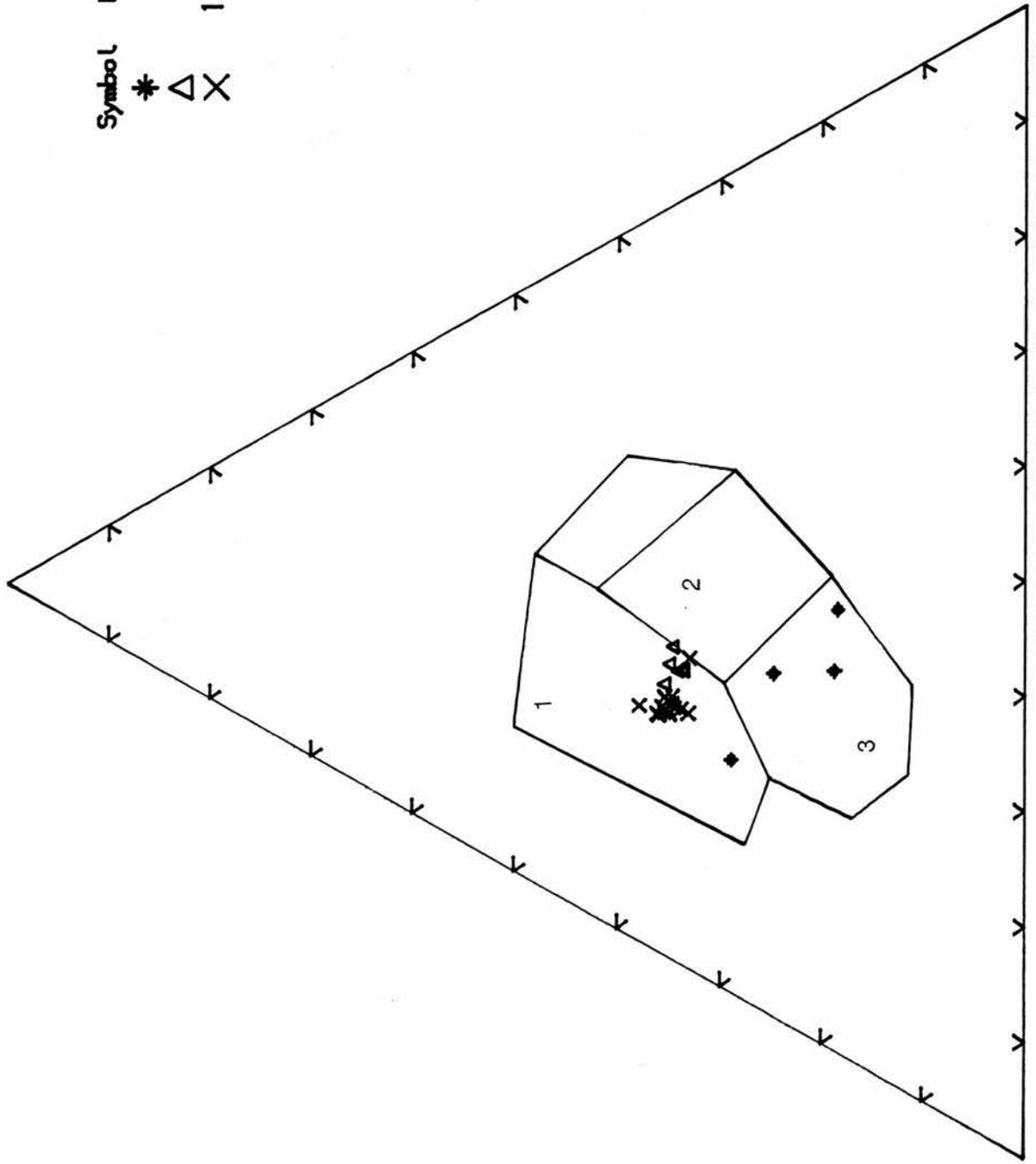
The work of Pearce & Cann (1973) has shown that the relative proportions of certain trace elements in volcanic rocks is diagnostic of the petrotectonic environment in which they were erupted. It has also been shown that these trace elements (Ti, Zr, Y, Nb & P) are

generally immobile during hydrothermal alteration and low grade metamorphism (Pearce & Cann 1973; Frey et al. 1974; Kay & Senechal 1976; Floyd & Winchester 1978). Some work has shown that the presence of carbon dioxide rich fluids can induce mobility in Ti, Y and Zr, (Hynes 1980) but this is not believed to have been significant in the Pinbain rocks, despite the extensive carbonate veining, for reasons that will be explained below.

When plotted on the Ti-Zr-Y diagram of Pearce & Cann (1973) (fig 5.1), the results fall almost entirely in the within-plate basalts field. The exceptions are from the high-silica group (see below), which show titanium and/or zirconium mobility, and contain too much silica to be considered as basalts in any case. The generally good grouping of these data suggests that either these elements have not been mobile during metamorphism, or that they have altered coherently, i.e. their original ratios have been preserved. The three points that plot outside the main group may have been affected by the increased mobility of these elements which Hynes (1980) has shown can be induced by the presence of carbon dioxide rich fluids.

The immobile trace element geochemistry of the Ballantrae Complex has been studied by several authors, e.g. Wilkinson & Cann (1974), Jones (1977) and Lewis & Bloxam (1977). Thirlwall & Bluck (1984) have summarised this work and presented their own results which indicate that the Pinbain lava sequence probably formed in an ocean island environment. This is in agreement with the results presented here, and since the same conclusion has been reached from the study of a variety of elements, i.e. Ti-Zr-Y (see above), rare earth elements

Ti/100



Symbol	N	Group
*	4	HSG
Δ	7	LTG
X	12	HTG

- 1-within plate basalts
- 2-MORB
- 3-calk-alkaline

FIG 5.1

Zr

Y\*3

(Lewis & Bloxam 1977), and Sm-Nd (Thirlwall & Bluck 1984), it seems likely that it is correct, and that the metamorphism of the basalts has not obscured their origin.

### 5.3 CHEMICAL CHANGES

The extensive growth of hydrous phases in virtually anhydrous basalts shows that fluids play an important part in low grade metamorphism. The fluids present in the rocks during metamorphism can be studied in several ways. Fluid inclusions trap small samples of the fluid, and fluid inclusion studies can provide information on the temperature of trapping, and to some extent on the composition of the fluids (see chapter 7). Stable isotope studies can be used to identify the origin of the fluids involved in alteration, and can also indicate the amount of fluid involved (see chapter 6).

The passage of large quantities of fluid through rocks during alteration leads to the possibility that the chemistry of the rock will be changed as the fluid brings in or leaches out some of the elements present in the rock. In the simplest possible case the extent to which the element concentration has been changed will depend on the amount of water passing through the rock, and might result in correlation between the volatile content of the rock and the concentration of the element concerned, assuming that : i) the concentration of the element has been changed by an amount greater than its original variation in the rocks, and ii) that the volatile content is related to the amount of water passing through.

The second assumption is probably false, because the volatile content will depend on the amount of hydrous minerals which have replaced the original anhydrous minerals and the nearly anhydrous basaltic glass. Thus the volatile content will reflect the degree of recrystallization, and this is not necessarily simply related to the amount of fluid moving through the rock. It is still, however, an indication of the amount of alteration, and thus it is important to note any correlations between loss on ignition, as a measure of the volatile content, and element concentrations. This technique was used by Mevel (1981) to determine major element mobility in Atlantic basalts.

The relatively constant composition of basalts from similar environments throughout the world allows us to compare the composition of spilites with unaltered rocks. As discussed above, the Pinbain lavas plot in the within-plate basalt field of Pearce & Cann (1973). Thirlwall & Bluck (1984) identified them as ocean island tholeiites. They show some evidence of mildly alkaline fractionation trends (Balsillie 1932) but additional evidence of their tholeiitic character is their low niobium/yttrium ratio, which is an indicator of tholeiitic character (Holub et al. 1984). This allows a comparison to be made between the Pinbain rocks and the mean composition of unaltered tholeiites, in order to determine the relative changes in composition which have occurred during alteration.

Alteration is not however the only factor which might cause variation in the concentration of elements in a suite of igneous rocks. Fractionation will result in either an enrichment of the element in the residual fluid, or a depletion if the element is preferentially taken up by the fractionating mineral phase. Since these rocks appear to be relatively uniform in terms of original petrography, it is unlikely that there will have been sufficient fractionation to enrich the incompatible elements (those which preferentially remain in the melt) by any great amount. Certainly, any enrichment of 100% or more would require another explanation - it would require 50% crystallization of the melt, which would produce major changes in the chemistry and petrography. However, fractional crystallization could remove very large proportions of an element from the melt, if the mineral has a high partition coefficient for the element concerned. The incorporation of phenocrysts from a different magma, which have already concentrated trace elements during their crystallization could lead to enrichments in the Pinbain rocks, but in the absence of specific evidence that this has occurred it must be considered unlikely.

The effects of fractionation can be taken into account if the element concerned is plotted on a graph with another element which is known to have been immobile. A correlation between the two elements would show that both have been affected by the same process, i.e. fractionation, so that the degree of fractionation of the rock controls the concentration of the element within the rock. If one element has been metasomatised then the correlation between the two

would be destroyed.

The graph of Ti-Zr-Y (fig 5.1) shows that these elements are not scattered, and thus have probably not suffered from metasomatism, because it would be highly unlikely that three elements would be metasomatised in such a way as to preserve relationships established by igneous fractionation. It is possible that they would behave similarly, but not in the same way as they did in the magma. Since the alteration process is not uniform, this would result in scattering on the diagrams. Since they are immobile, these elements are suitable for comparison with the other elements. An example of a graph showing good correlation, i.e. immobility of the elements during alteration, is that of titanium against zirconium, fig 5.2, where the concentrations of the two elements fall on a straight line. The zirconium and titanium concentrations will be used as fractionation indexes for determining the mobility of the other elements.

#### 5.3.1 Major elements

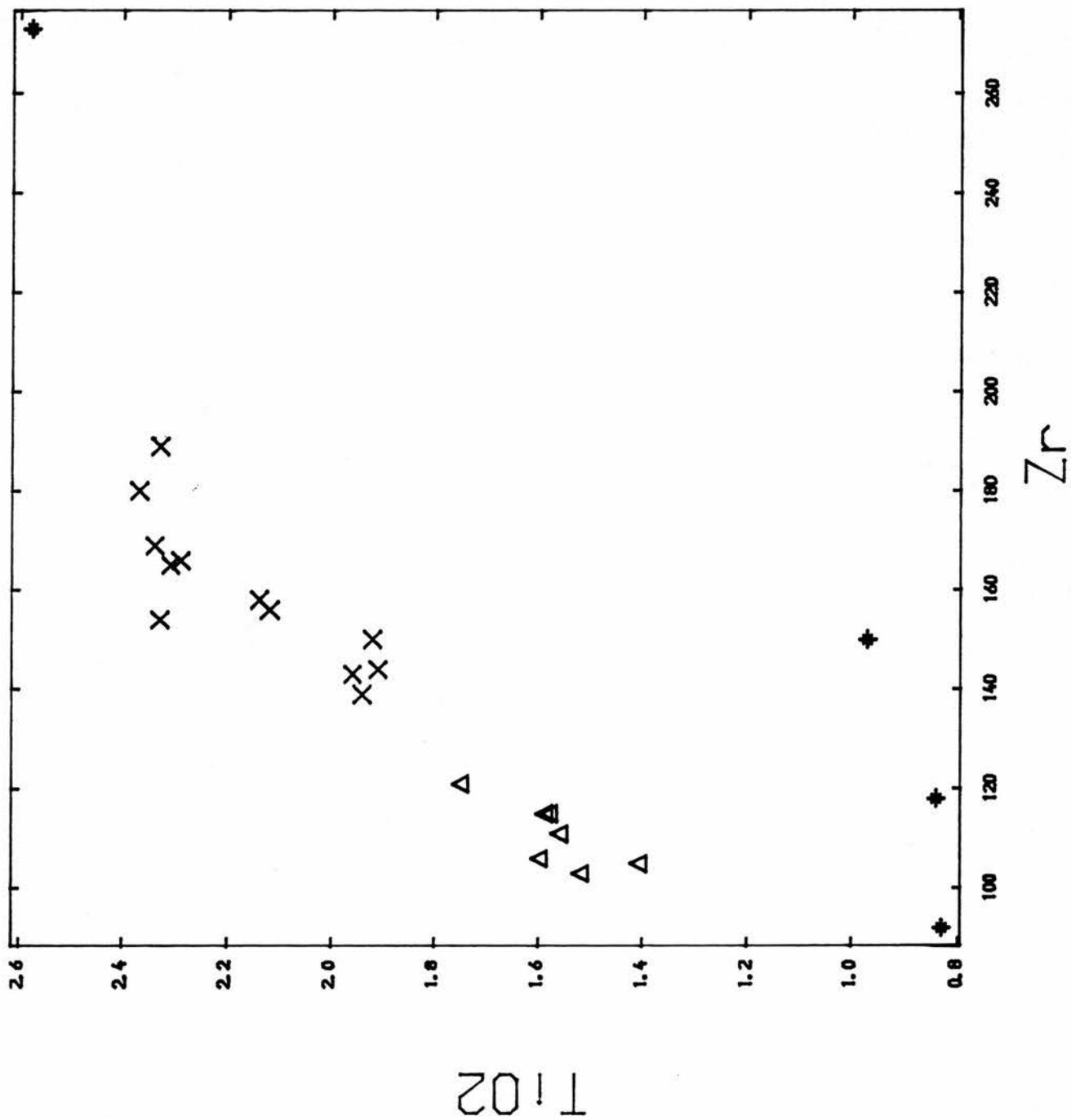


FIG 5.2

#### 5.3.1.1 Fractionation

The validity of these discussions rests on the basis that the Pinbain succession is a group of related rocks which had similar compositions prior to alteration. If this is true then variations in the original chemistry would have been caused by fractional crystallization, and different elements would change in a definite relationship to each other, i.e. they would form a line if plotted on a graph against each other. As was explained above, zirconium was chosen as an index of fractionation, because it is immobile in these rocks.

The graph of zirconium against titanium (fig 5.2) shows the sort of correlation which would be expected in an unaltered rock. It forms a good line, with the exception of four points. In the histograms of major element concentrations (fig 5.14), these samples are distinguished by special symbols, and it can be seen that they have unusual compositions, particularly high silica, and low magnesium and calcium. These unusual samples probably represent either extremes of alteration, in which even the titanium and/or zirconium have become mobile, or contaminated samples containing vein or sedimentary matrix from a breccia. The alteration hypothesis seems most likely because the potassium, phosphorus and manganese contents are relatively normal. The possibility that they are fractionates can be ruled out because although the high silica and low magnesium content could be a linked fractionation change, there is no consistent change in the aluminium, titanium and iron contents, while the sodium and calcium changes are too extreme to be caused by the same process. It is

possible, however, that these were relatively acidic fractionates before alteration, which would help to explain why the silicon, calcium, magnesium and sodium values are extremes for the whole succession. This group will be referred to as the high-silica group, or HSG.

The zirconium-titanium diagram shows that although the points all plot on or close to the same line, there is a distinct division into two groups, one with low titanium and zirconium, and the other high. These groups will be referred to as the high-titanium group (HTG) and low-titanium group (LTG), and they have been given different symbols in the figures. They are important because they show that there were originally two groups of lavas. This is reflected in the bipolar appearance of many of the histograms, for both major and minor elements, and in particular for iron and magnesium. The two groups are distinguished petrographically, in that the low-titanium group contains little or no pyroxene, whereas the high-titanium group contains much pyroxene, which is of titan<sup>a</sup>augite composition (chapter 4). The differences in titanium, zirconium, iron and magnesium must therefore be the result of titan<sup>a</sup>augite fractionation, with those samples which have retained their titan<sup>a</sup>augite forming the HTG, while those in which the titan<sup>a</sup>augite was removed prior to eruption are relatively low in its constituent elements.

With the exception of the four HSG samples discussed above, the zirconium/titanium diagram shows that the fractionation index concept works for these elements, and they can be considered to be generally immobile within the succession. However, when the other elements were

plotted against zirconium, only three showed a correlation, while the others were scattered. The two that showed good correlation were iron (fig 5.3) and phosphorus (fig 5.4), while manganese showed a reasonably good grouping (fig 5.5), apart from the four anomalous HSG samples discussed above. Manganese has a very limited range of composition, and the fact that it forms a group rather than defining a line is probably due to its not fractionating to any great extent, rather than to alteration.

Although the iron-zirconium correlation is good, there is some degree of scattering. This is clearer on the iron-titanium diagram (fig 5.6), which indicates the scatter is to both sides of the line. It is not possible to say whether this scattering is due to alteration, or to igneous processes, but if it is alteration there is no consistent trend towards either enrichment or depletion. The distinction between the HTG and the LTG are clear on these diagrams, while the HSG does not follow the trend, again indicating the separateness of these samples.

The magnesium-titanium diagram (fig 5.7) has a slight suggestion of correlation, and it can be seen that there is a distinct difference in magnesium content between the LTG and the HTG, which supports the origin of these groups by titanite fractionation. There is also a large amount of scatter which indicates that magnesium has probably been mobile in many, if not all, of the samples. Although the correlation is poor, the general impression is that the aberrant samples lie below the magnesium-titanium fractionation line, which means that magnesium has generally been leached out of the Pinbain

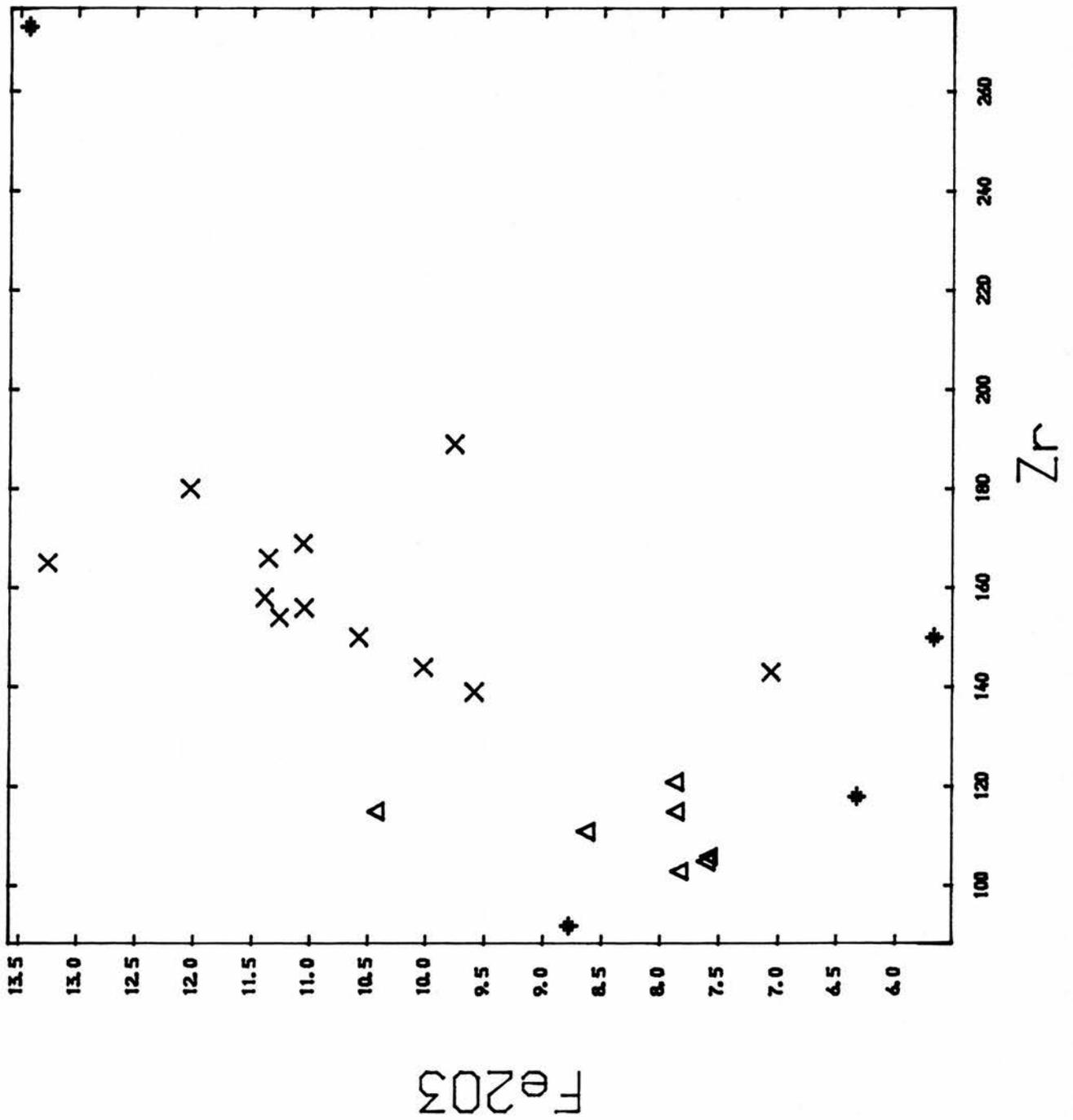


FIG 5.3

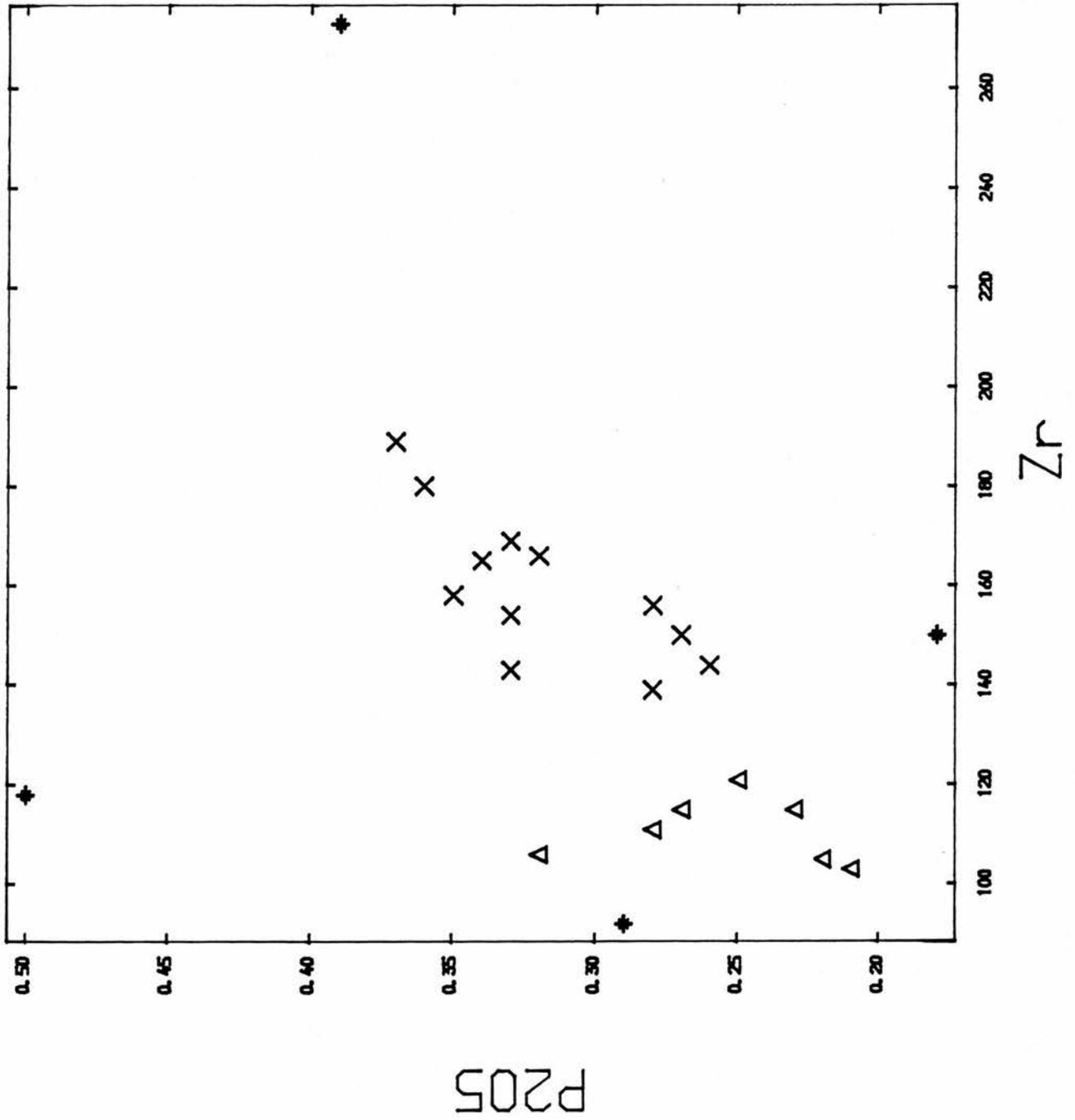


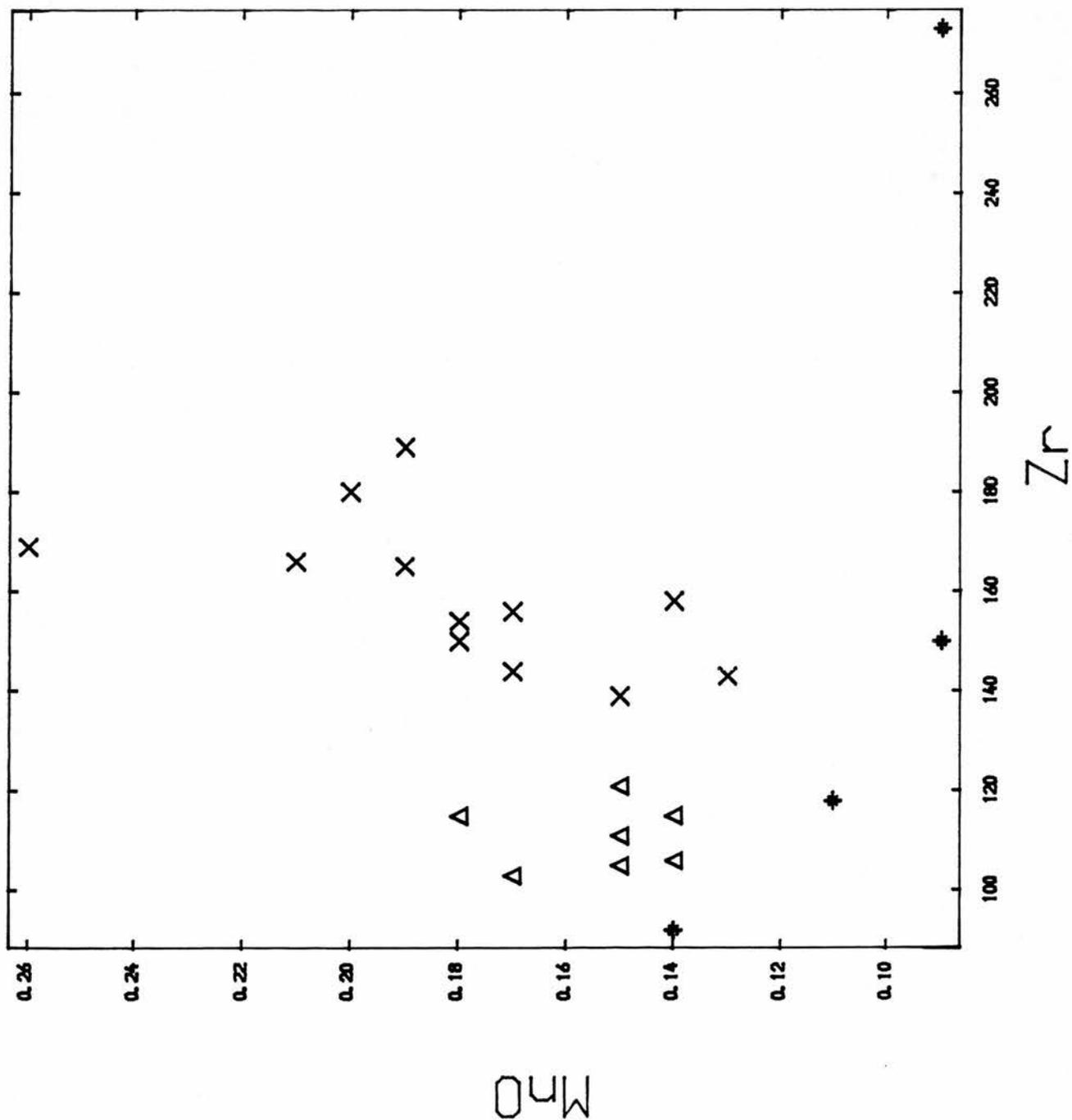
FIG 5.4

P205

Zr

Symbol	N	r	Group
◆	4	-0.73	HSG
△	7	-0.04	LTG
X	12	0.59	HTG

FIG 5.5



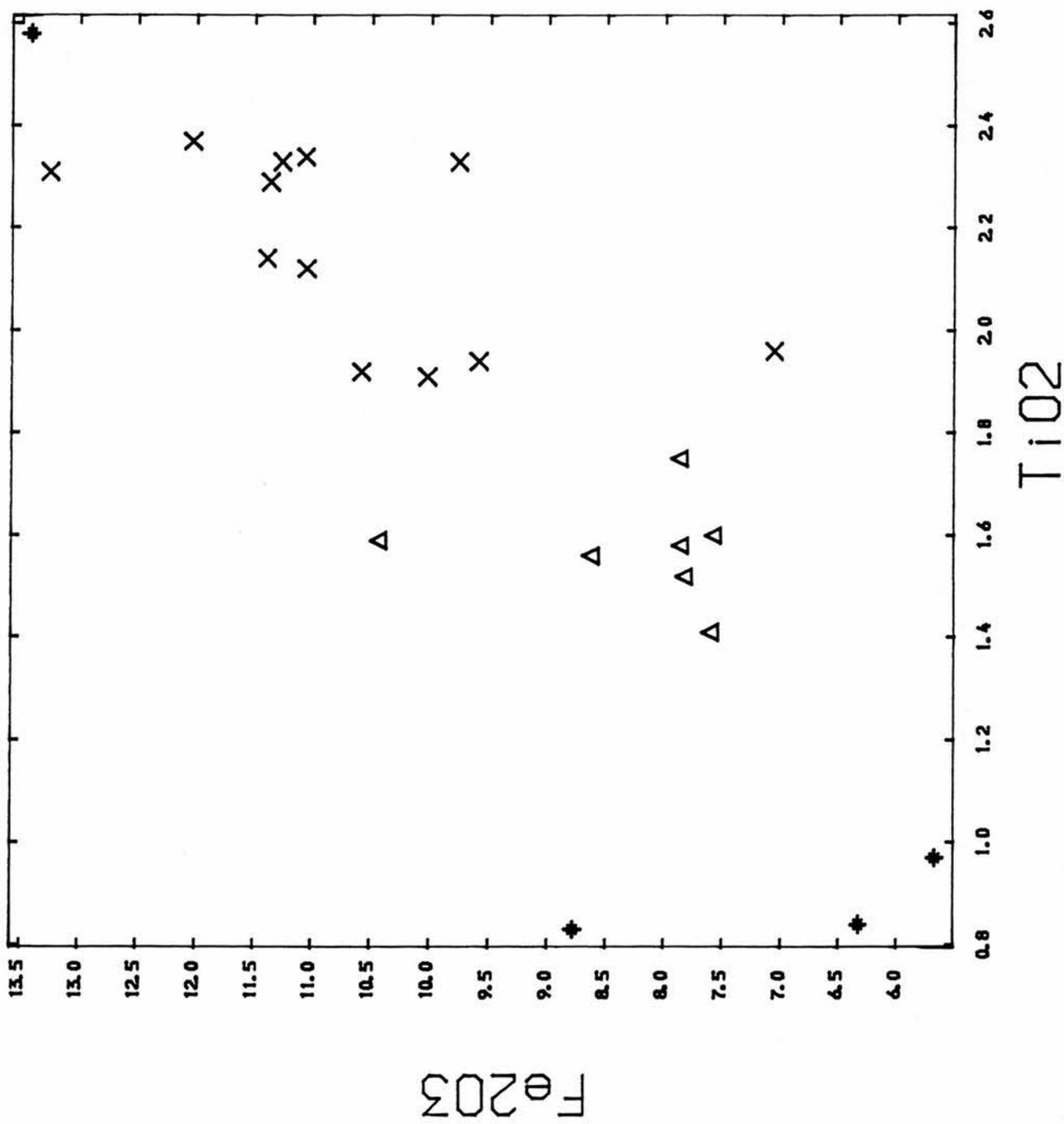


FIG 5.6

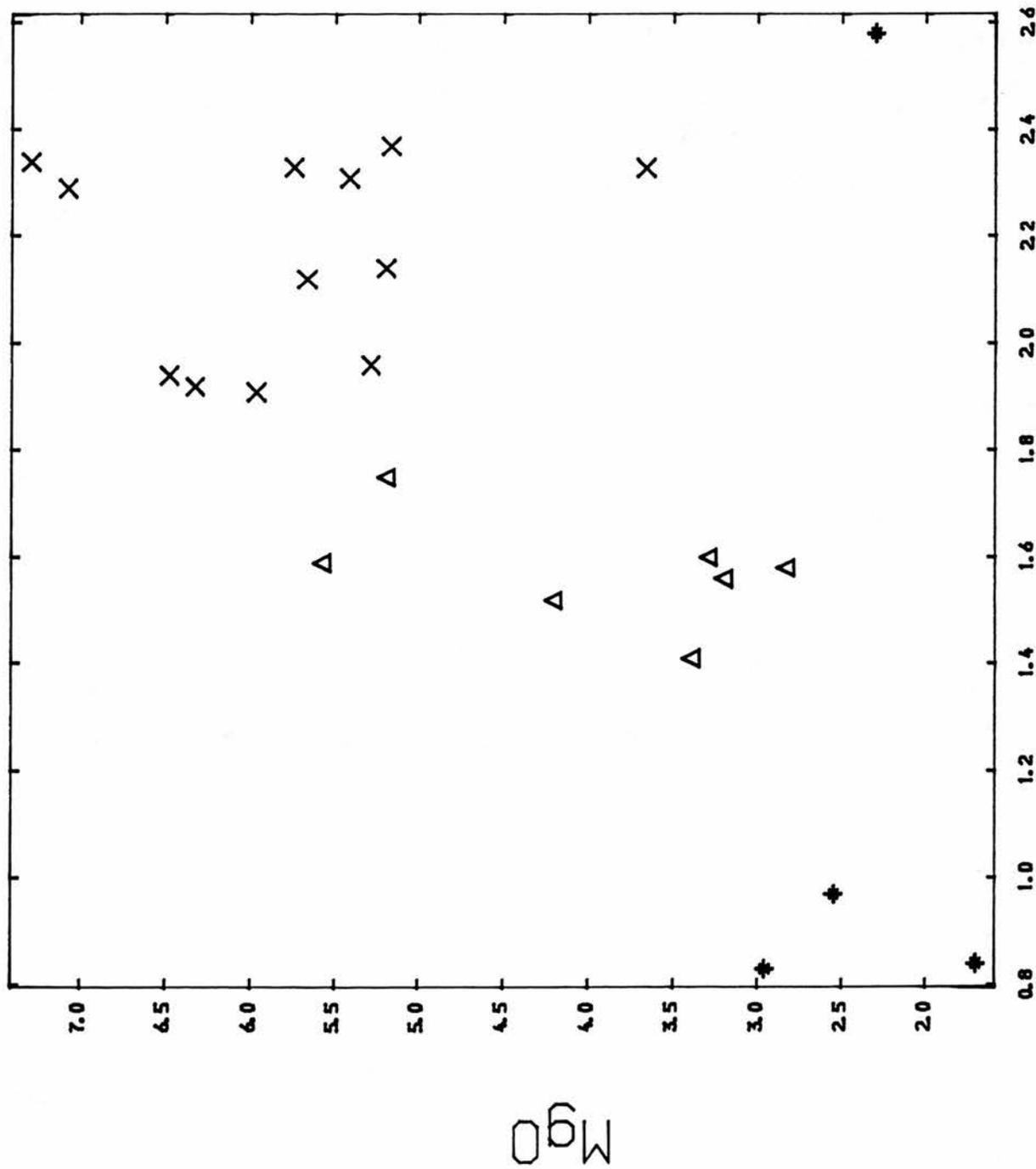


FIG 5.7

TiO<sub>2</sub>

MgO

rocks. The iron-magnesium graph (fig 5.8) shows a considerable degree of scatter, rather than a good correlation between iron and magnesium within each group, as would be expected in a normal igneous trend, again suggesting that magnesium has been somewhat mobile (iron correlates with titanium and is therefore not mobile). This will be discussed further in the section on iron and magnesium below (section 5.3.1.3.4).

The HSG is again different from the remainder of the samples, emphasising the fact that it must be considered separately from the other samples in the Pinbain block.

From this, it appears that there is no evidence that any of the major elements was completely immobile, although the iron, manganese and phosphorus concentrations are in general consistent with immobility. Titanium shows the least mobility, although there are still four samples which show anomalous behaviour for titanium and/or zirconium.

#### 5.3.1.2 Water-related alteration

The graph of silica against loss on ignition (fig 5.9) does not show a very clear correlation, but there is a slight indication that the samples with a higher loss on ignition tend to have lower silica values. This may indicate that silica has been leached from these rocks during the alteration process. It does not appear that any

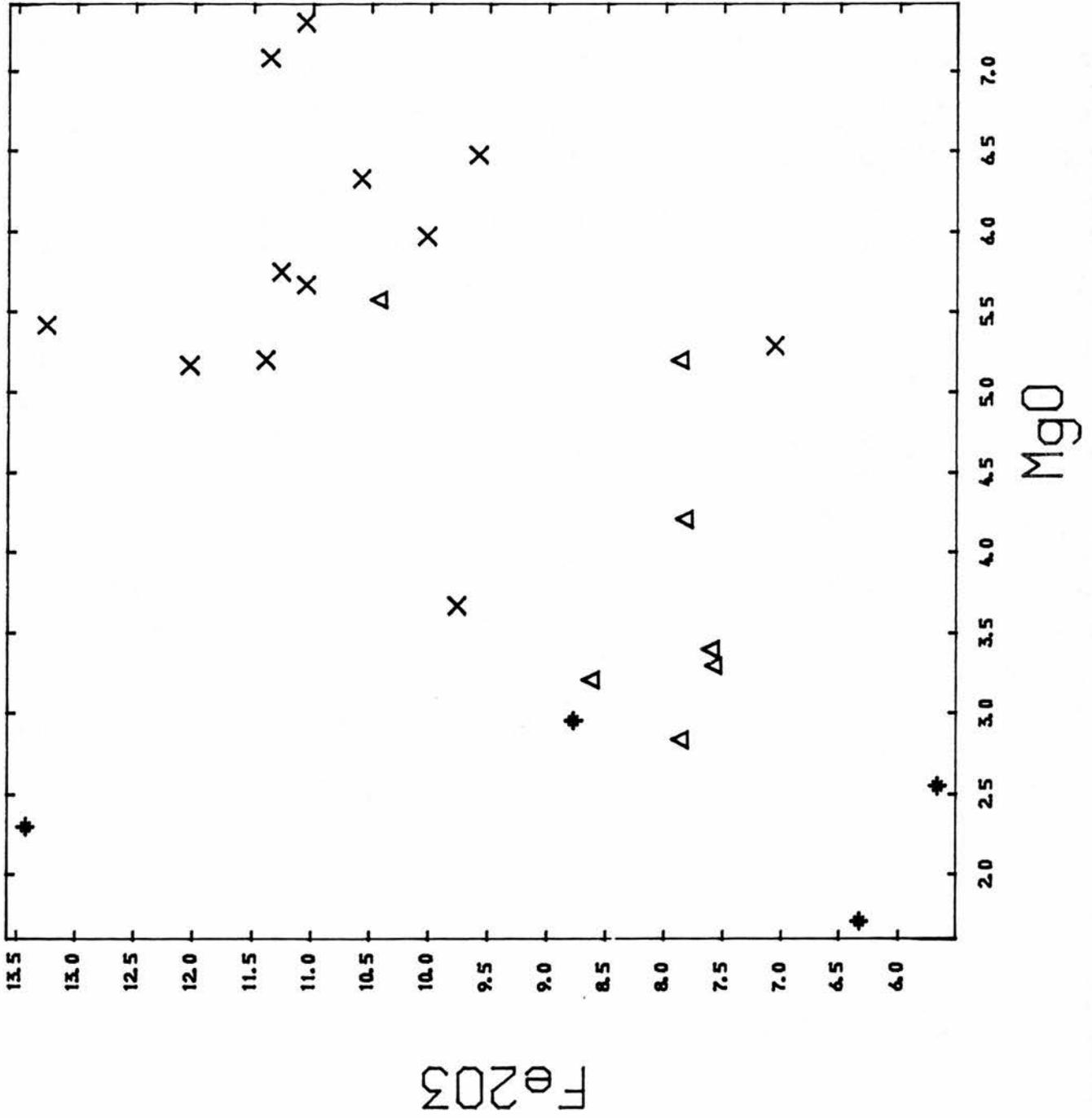
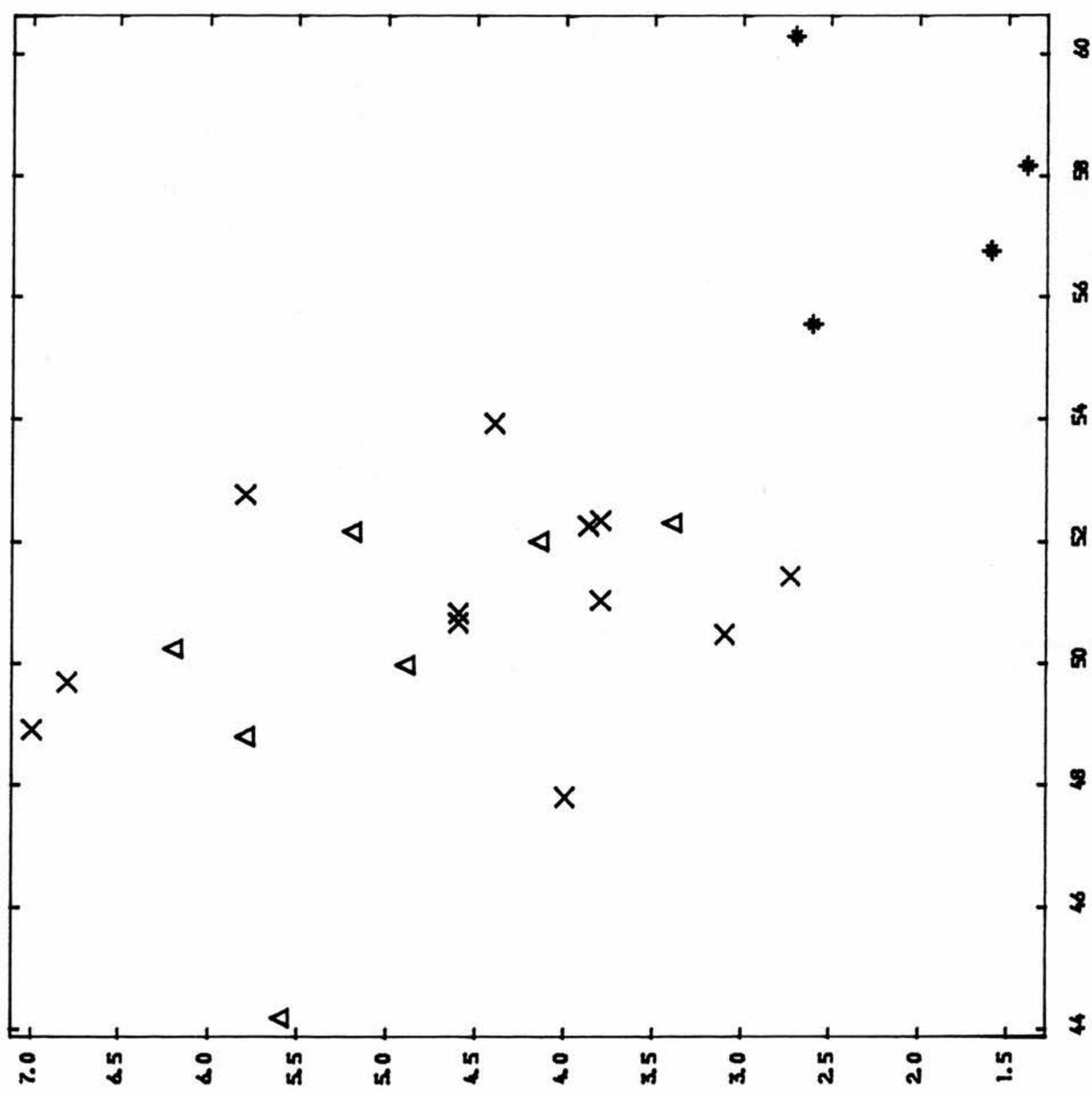


FIG 5.8



Symbol	N	r	Group
◆	4	0.16	HSG
△	7	-0.54	LTG
×	12	-0.26	HTG

FIG 5.9

SiO2

SiO3

depletion which has occurred has been large, high loss samples possibly having about 2% less silica than the low loss samples (with the exception of the HSG, which differ in many ways from the rest of the samples. The amount of scatter in the diagram may result from the superimposition of alteration on original igneous variation.

Although titanium is immobile the graph of titanium against loss (fig 5.10) is interesting because the low-titanium group has a rather higher loss than the bulk of the high-titanium group. Since these groups have been identified as primary igneous features, it appears that the chemical differences between them, i.e. the iron, magnesium and titanium contents control the volatile content. This will be discussed further below, in the major element conclusions (section 5.3.1.4).

The graph of iron against loss on ignition (fig 5.11) appears on first sight to show a negative correlation, which would indicate that iron has been progressively depleted with increasing loss. However, when the HTG and LTG are considered as separate groups it can be seen that there is no correlation within each group, and the apparent correlation appears because the LTG has higher volatile contents than most of the HTG. There does not appear to be any correlation between iron content and loss on ignition within each group, and so there is no evidence from this plot that iron has been mobile.

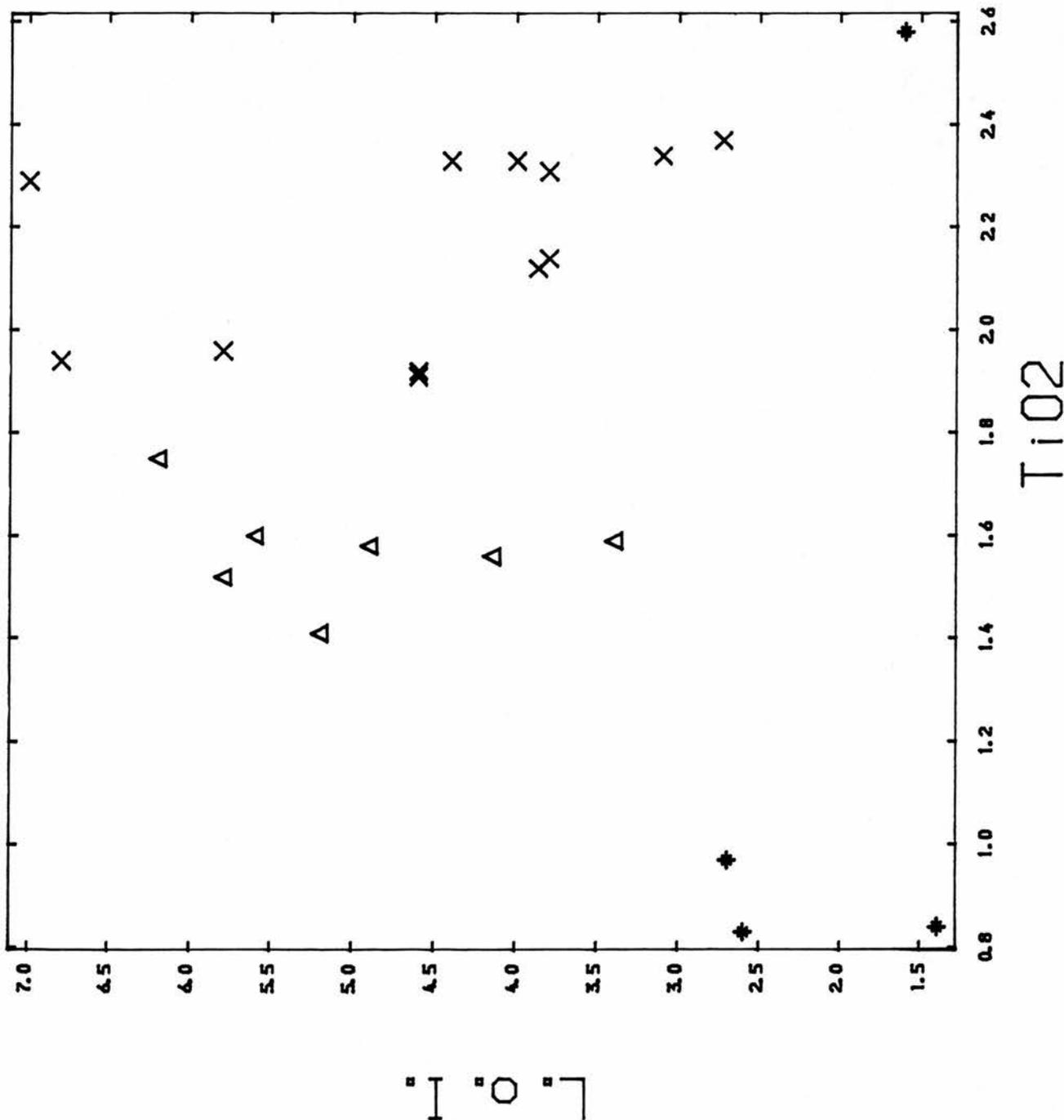


FIG 5.10

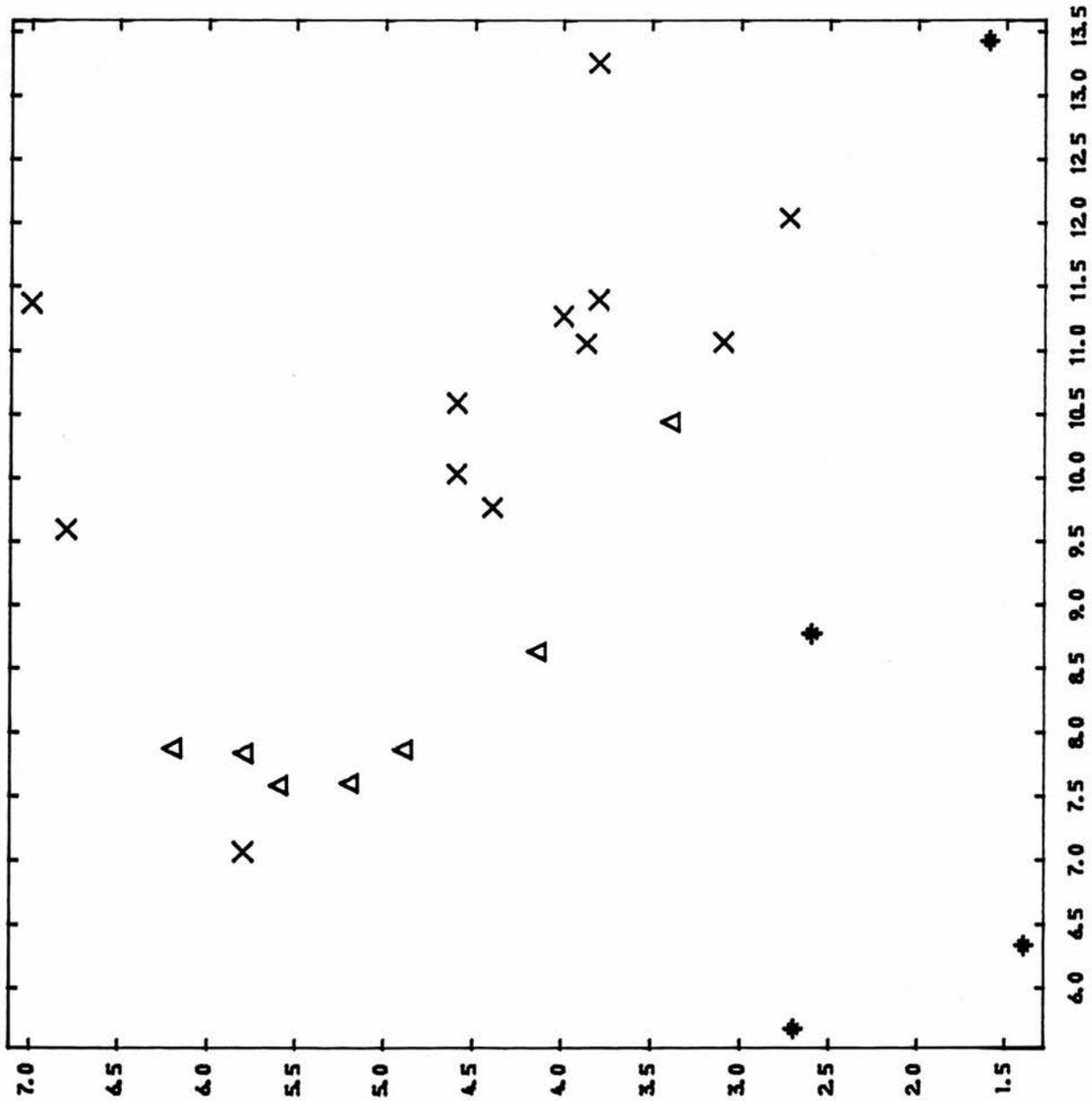


FIG 5.11

Fe<sub>2</sub>O<sub>3</sub>

The HSG do not plot with the two main groups, having a lower loss on ignition, but a widely variable iron content.

Magnesium behaves in a similar manner to iron (fig 5.12). The LTG samples have higher volatile contents than the bulk of the HTG, showing that the magnesium and iron contents are closely linked by the original igneous variation in chemistry.

The graph of calcium against loss (fig 5.13) does not show any clear correlation with loss, but the highest calcium values occur in samples with a relatively high loss. In the case of calcium it is possible that the high calcium values are a result of the presence of calcite, and the high loss value is partly due to carbon dioxide, rather than water.

#### 5.3.1.3 Comparison With Normal Basalt

The Pinbain lavas have a chemistry which classifies them as ocean island tholeiites (section 5.2). Wilkinson (1986) has given an average composition for 1089 tholeiitic basalts, which is given below, along with an average for the Pinbain rocks, and the range for each element.

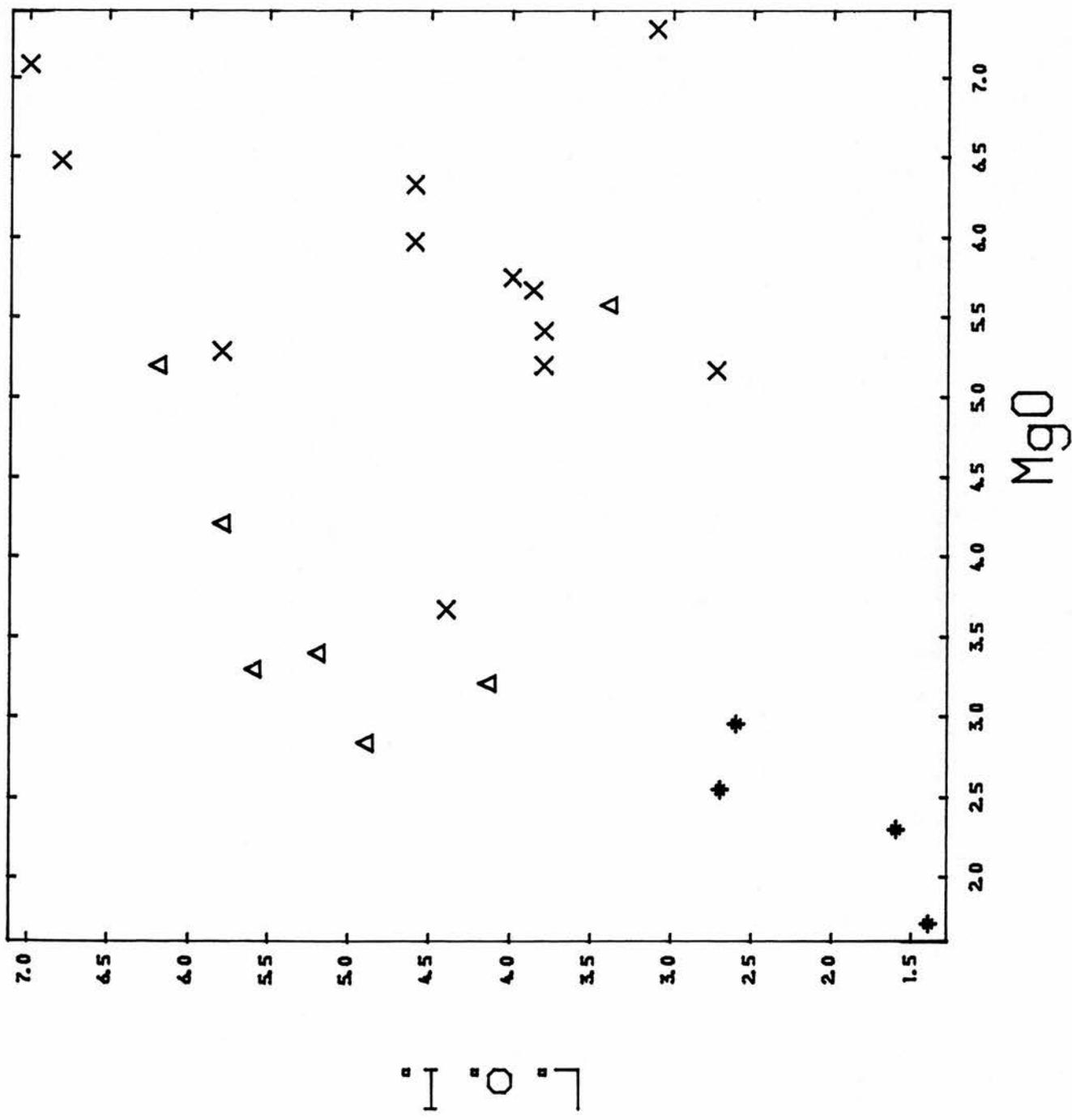


FIG 5:12

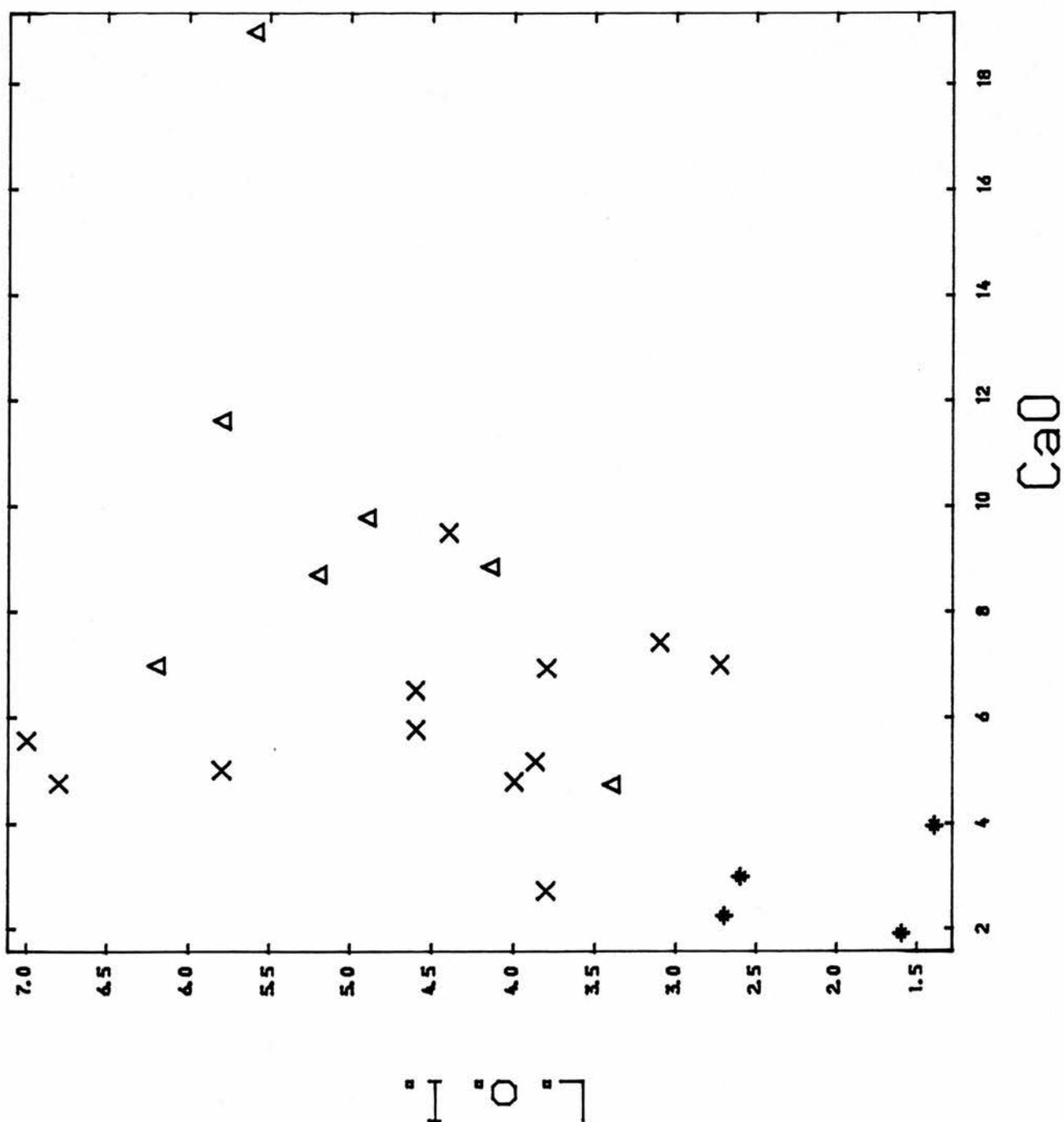


FIG 5.13

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	MEAN	MEAN	RANGE
	THOLEIITE	PINBAIN	PINBAIN
SiO <sub>2</sub>	50.36	51.06	47.82-53.94
TiO <sub>2</sub>	2.00	1.97	1.41-2.37
Al <sub>2</sub> O <sub>3</sub>	14.22	17.69	14.10-20.64
Fe <sub>2</sub> O <sub>3</sub>	12.78	9.95	7.07-13.43
MnO	0.12	0.17	0.13-0.25
MgO	6.78	5.22	2.84-7.30
CaO	10.78	6.79	2.74-11.64
Na <sub>2</sub> O	2.38	5.86	3.79-8.30
K <sub>2</sub> O	0.38	1.00	0.13-2.89
P <sub>2</sub> O <sub>5</sub>	0.20	0.29	0.21-0.5
LOSS	----	4.67	2.73-7.00

---

The samples used to compile this table exclude 4 which have silica values of over 55%, and are therefore not comparable with basalts. This high-silica group shows other chemical differences, which were discussed above. One other sample was omitted because it had a silica value of only 44.2%, and a calcium value of 18.99%, which suggests that the sample was contaminated with calcite which was not removed before it was analysed.

As can be seen from the table, and from the histograms of major element concentrations (fig 5.14), the major element chemistry of these spilites differs from that of normal basalts in several ways.

#### 5.3.1.3.1 Silica

The average silica content is slightly higher, and in some specimens much higher than in the average basalt. The four samples with very high silica contents have zirconium and/or titanium contents that are different from the rest of the rocks, and this suggests that these samples have been highly altered. If these samples are removed from the discussion, along with the low-silica sample which is contaminated with calcite, then it can be seen that the histogram for silica content is quite tightly constrained, with an average close to that for normal basalts. This would suggest that the silica content has not been altered. However, the silica content is highly scattered, and shows no relation to the zirconium content (fig 5.15). It is therefore likely that silica has been mobile within the Pinbain rocks, but there has not been a large change in the silica content of the succession as a whole. There is some quartz veining in the Pinbain Block (chapter 2), indicating that fluids passing through were carrying silica.

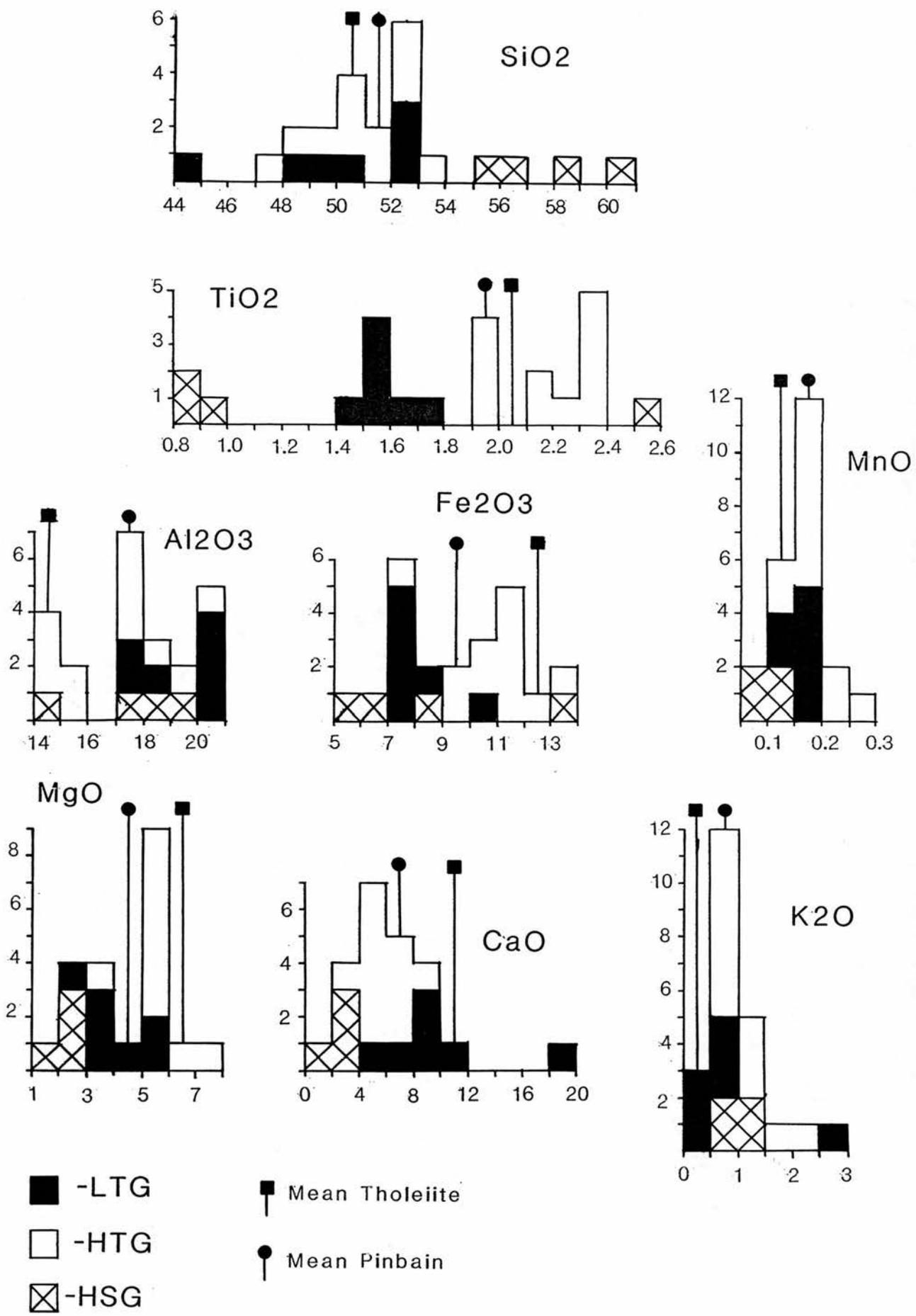


FIG 5.14. Histograms of major element concentrations (wt. %).

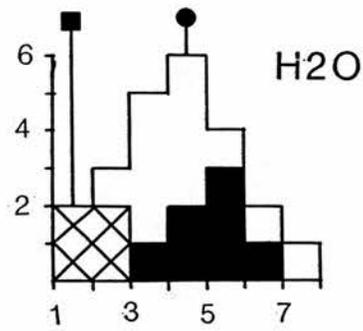
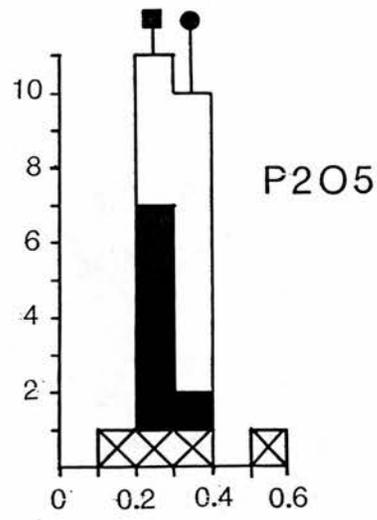
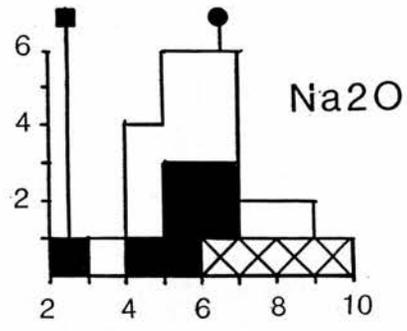


FIG 5.14. cont.

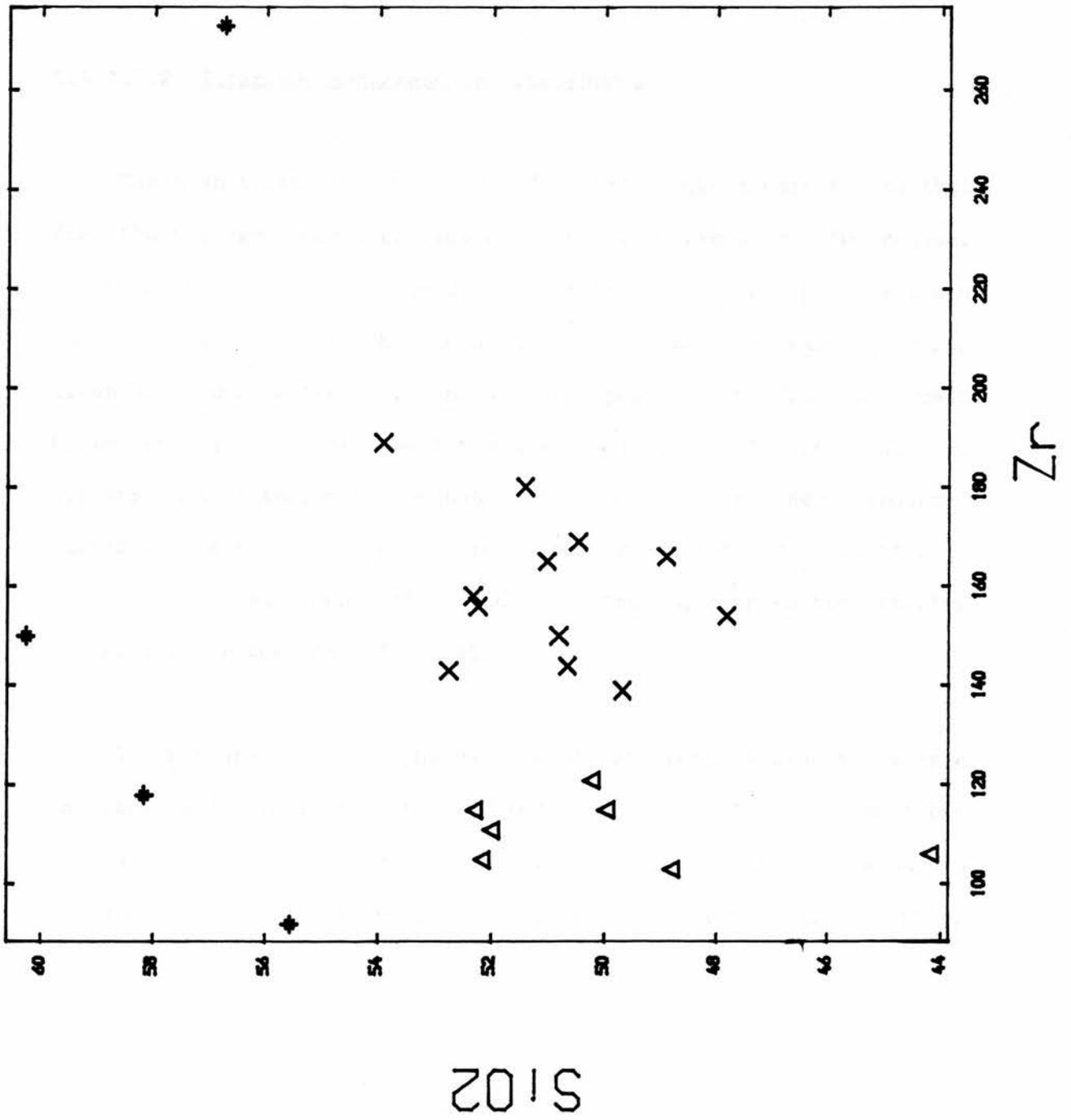


FIG 5.15

The silica histogram is bipolar, but the bipolarity is not related to the division into the HTG and LTG. The bipolarity may represent an original igneous pattern, but since there is no correlation between silica and zirconium this cannot be proved. The histogram shows a tailing towards the low silica side, which may have been produced by alteration, because the iron and magnesium contents are rather low for these silica values, and there is good evidence that iron at least has been relatively immobile (section 5.3.1.1).

#### 5.3.1.3.2 Titanium, Manganese and Phosphorus

The mean titanium content of the Pinbain rocks is similar to that for the average tholeiite. The histogram is divided into two groups, which can be related to differences in petrography, and to variations in other aspects of the chemistry. The four extreme values for titanium are from the HSG, and as they plot apart from the main histogram, and also off the titanium-zirconium correlation trend, it appears that titanium has probably been mobile in these abnormal samples. The histogram appears to be poorly constrained, but this is a result of an expanded scale. Excluding the HSG samples the titanium values fall in the range 1.4-2.4%.

The manganese and phosphorus contents are both similar to average basalts, and have tightly constrained histograms. They can therefore be considered to be largely immobile, particularly since they show a correlation with zirconium (section 5.3.1.1). The HSG samples which

are marked on the histogram include an anomalous sample for phosphorus. This supports the suggestion that the HSG has been more highly altered, with more elements showing mobility, than the majority of the rocks.

#### 5.3.1.3.3 Aluminium

The aluminium content of the Pinbain rocks is considerably higher than the average, indeed, the bottom of the range of aluminium values is only just lower than the average tholeiite. The higher values of aluminium are too high to be found in rocks of this type - only island-arc type basalts have aluminium contents this high (Wilkinson 1986), and there is no evidence that these rocks are in any way connected with an island arc source (Thirlwall & Bluck 1984). The high silica samples which are distinguished on the histogram do not form extremes, as might be expected if they were fractionates. It is therefore probable that aluminium has been enriched during the alteration process.

The aluminium histogram is trimodal. The HTG generally contain the least aluminium, including all those samples with values around the normal average for tholeiites. It is probable that the original aluminium distribution was bimodal, with peaks possibly at 14-15%, and 17-18%, but that aluminium has also been added to the rocks to produce the present pattern. Since the HTG contain the lowest amounts of aluminium it is probable that the original pattern was caused by the same fractionation process which produced the HTG and LTG, i.e. that

aluminium became more concentrated as a result of pyroxene being removed. The pattern has been modified by aluminium metasomatism.

#### 5.3.1.3.4 Iron and Magnesium

Iron shows a good correlation with zirconium and can therefore be considered to be relatively immobile (section 5.3.1.1). The histogram shows a bimodal pattern, with the lowest concentrations of iron being considerably below that of the average tholeiite. The iron-zirconium diagram (fig 5.3), however, shows that these are genuine igneous values, produced by fractionation, rather than by alteration, apart from the two lowest values, which are from HSG samples which do not plot on the titanium-zirconium line. The lower iron values would be compatible with rocks containing slightly more silica than any of the present samples do, apart from those which do not plot on the titanium-zirconium line. This may indicate that silica has actually been leached from these rocks, although there is no direct evidence for this (see above).

Magnesium shows little correlation with zirconium, thus indicating that it has probably been mobile. The histogram shows a similar pattern to that for iron, in that it is bimodal, with one peak at slightly less than that for normal basalts, and another which is extremely low for rocks of this sort. The lowest magnesium values come from the HSG, and this suggests that the low magnesium values are a result of leaching during alteration. However, since the iron content shows a similar pattern, and yet preserves its correlation

with zirconium, it is probable that the pattern is an original igneous one, and the degree of magnesium mobility has not been sufficient to destroy it. As can be seen from the magnesium-zirconium (fig 5.16) and magnesium-titanium (fig 5.7) diagrams, a rough correlation can be drawn if some of the samples are assumed to be altered and are removed.

The lower magnesium values recorded in these rocks, 3-4%, are rather low to be found in association with the silica values recorded. This is similar to the situation for iron, and is indirect evidence that either silica has been depleted, or that iron and magnesium have been removed, and the iron-zirconium correlation is spurious. The depletion of silica seems most likely, since the silica-zirconium diagram (fig 5.15) is extremely scattered, and so silica must have been mobile.

#### 5.3.1.3.5 Calcium

Calcium in the Pinbain rocks is much reduced in comparison to the average tholeiite, and the histogram is relatively broad, and displaced towards zero relative to the average tholeiite. This suggests that the calcium has been depleted in these rocks. This would be expected, since the calcium is expelled from feldspar during spilitisation. Much of the calcium may remain within the succession, but in the form of calcite in veins, which is largely removed from the specimens before analysis. (However, fluid inclusion evidence suggests that most of the large carbonate veins were derived from

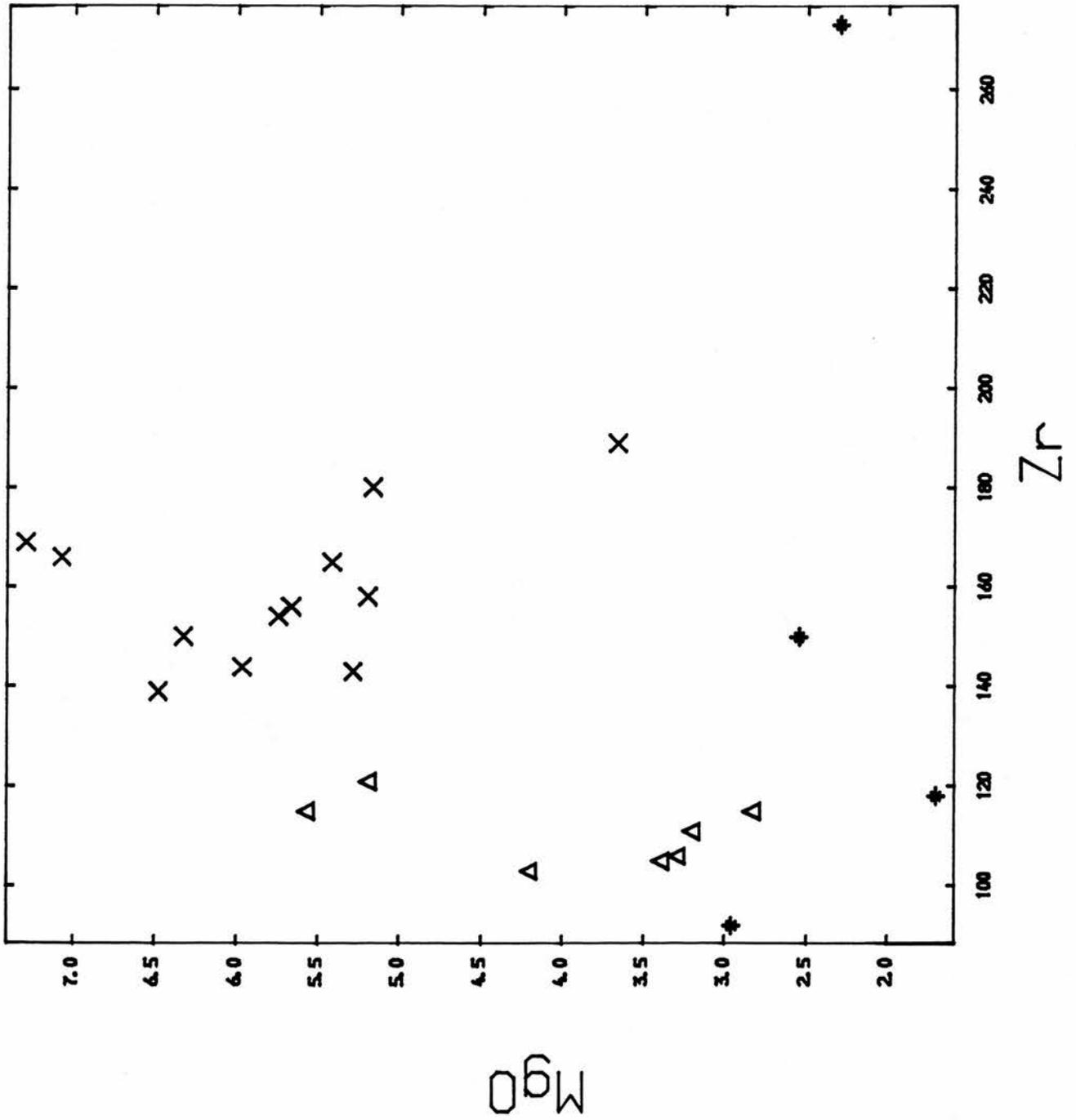


FIG 5.16

outside the succession - see chapter 7). The four high silica samples have the lowest calcium contents, again suggesting that these are the most highly altered rocks.

#### 5.3.1.3.6 Sodium

Perhaps the most obvious difference between the Pinbain rocks and the average tholeiite is the sodium content, which is nearly tripled in the Pinbain rocks. The histogram is similar to that for calcium, in that it is rather broad, and the normal average is only at one extreme of the histogram. This enrichment of sodium is the basic chemical difference between a spilite and a normal basalt, and it reflects the replacement of labradorite feldspars by albite. The extra sodium required for the change is derived from sea-water.

#### 5.3.1.3.7 Potassium

The histogram for potassium is quite well constrained, with most samples showing between 0 and 1.5% potassium. The average for Pinbain is slightly higher than that for normal tholeiites, but the tholeiite average includes many low-potassium tholeiites (Wilkinson 1986), which mean that the average for ocean-island tholeiites alone would be higher, and so the Pinbain average is probably not significantly different from ocean island tholeiites. The histogram however does show a slight tailing towards the high side, with the high values not being in the high silica samples. This suggests that potassium has

been introduced to these samples. The mobility of potassium is indicated by its lack of correlation with zirconium, and since some samples show potassium feldspar replacing labradorite, and some potassium feldspar veining (chapter 2), the potassium in the Pinbain rocks must have been mobile, although there has only occasionally been a bulk change in the potassium content. Rubidium shows a very similar pattern to potassium (section 5.3.2.3.1), as might be expected from their general chemical similarity.

#### 5.3.1.3.8 Volatiles

The final major difference between the Pinbain rocks and the average tholeiite is the high loss on ignition, indicating a high volatile content, i.e. water and carbon dioxide. A value for an average tholeiite would be about 1.4% (Le Maitre 1976). This is the minimum value in the Pinbain rocks, with the average value being 4.26%. This change is also characteristic of spilites as a whole, and is accounted for by the hydrous minerals such as chlorite which grow in the previously almost anhydrous basalt. The water needed is supplied by sea water moving through the succession. There is also a certain amount of carbonate in the rocks, which cannot be removed before analysis, occurring as small veins, and also as an alteration product of plagioclase.

The histogram, and the iron-loss diagram (fig 5.11) indicate that the high-titanium group generally have a lower volatile content than the low-titanium group. As discussed above, it appears that the composition controls the volatile content, rather than vice-versa. The possible reasons for this will be discussed in the major elements conclusions (section 5.3.1.4).

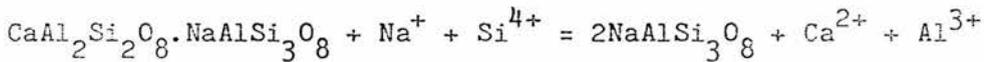
The high-silica group are unusual in terms of their volatile content, as they are for many other elements. Despite having unusual, and presumably highly altered chemistries, they have the lowest losses on ignition, less than twice that expected for unaltered rocks. This means that their degree of alteration is not dependant on the volatile content, and presumably a special set of processes must have been operating in these rocks.

#### 5.3.1.4 Major Conclusions

The evidence presented above shows that several of the major elements have been noticeably metasomatised during the very-low-grade metamorphism which has affected these rocks. The only elements which are generally immobile are titanium, phosphorus, manganese and iron. Potassium has probably been immobile in the majority of the samples, although some may show a slight enrichment. Magnesium may have been slightly depleted, but not to any major extent. Of the other elements, silicon has probably, and calcium has definitely been depleted. Aluminium and sodium have been added to the rocks, and the

volatile content has been greatly increased.

The extensive alteration of the composition of these rocks is not surprising when it is considered that they have been extensively reconstituted mineralogically, at the same time that large quantities of fluid were passing through the rocks. During the mineral reactions, virtually all the elements must be mobile, at least locally. Of the main changes which take place, the replacement of labradorite by albite involves the removal of calcium and aluminium from the mineral, and its replacement by sodium and silicon. The sodium is derived from sea-water, while the silicon is probably derived from the matrix of the lavas. The calcium is removed from the rock, much of it probably going to form calcite in veins, while the aluminium appears to be retained in the rock, probably in chlorites and clays growing in the matrix. The reaction taking place is as follows :-



The increase of sodium and decrease of calcium within these rocks can be linked directly to this reaction. The graph of sodium against calcium (fig 5.17) shows that there is a broad negative correlation, showing that changes in calcium and sodium content are linked. The graph also shows that there is no difference between the HTG and LTG in terms of the behaviour of their sodium and calcium chemistry. This shows that it is entirely an alteration effect, and is not controlled by the pre-existing variations in chemistry.

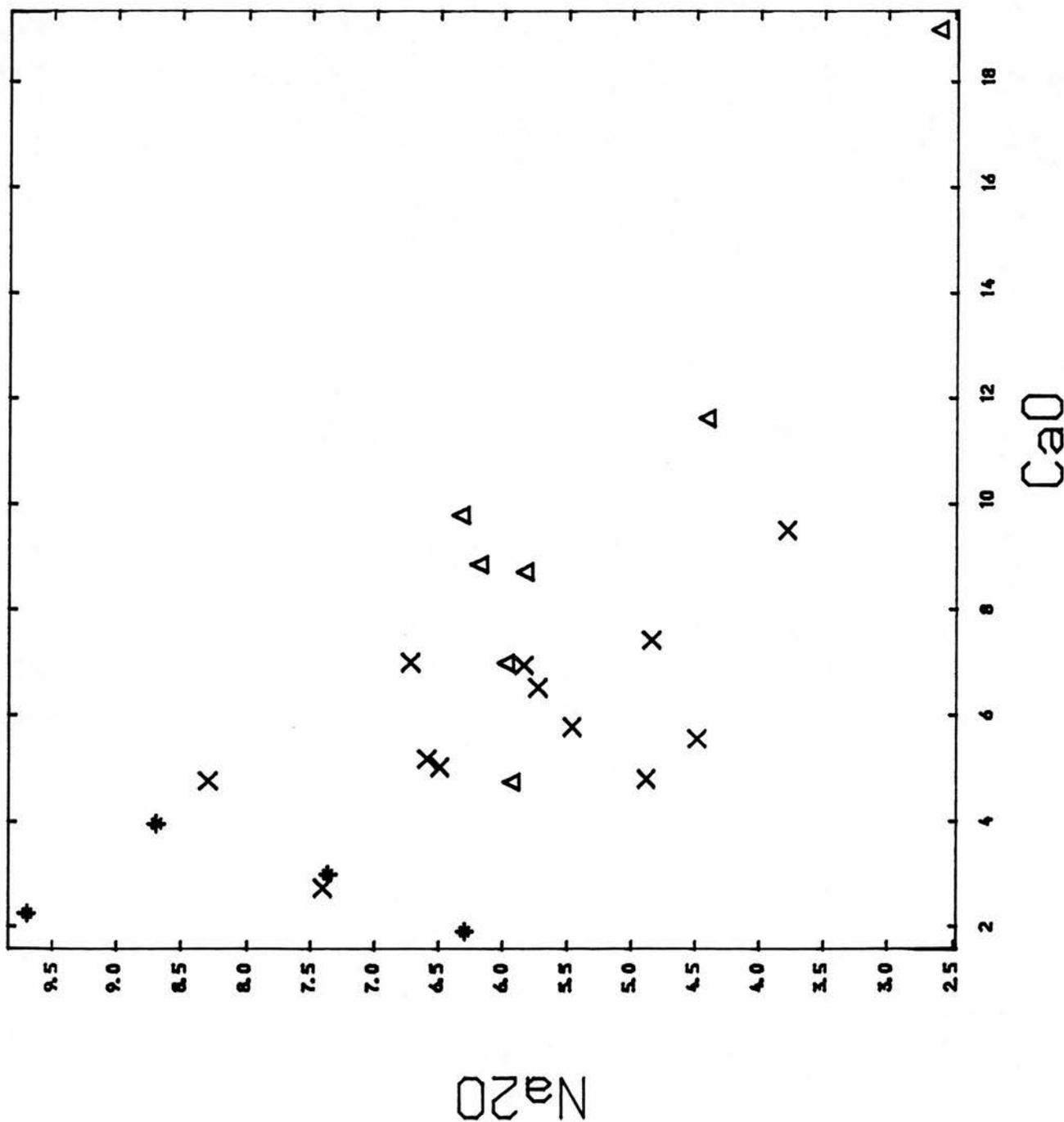


FIG 5;17

The second major change has been the growth of chlorite and sphene in the matrix, which was originally composed of volcanic glass of no fixed composition. To enable the growth of the new phases there would have to be a redistribution of iron, magnesium, aluminium, silicon, calcium and titanium, although these elements would be present in the matrix and would not necessarily have to move very far. In addition, water would have to be introduced to fill the hydroxyl sites in the chlorite.

Although elements have to be mobile on a local scale to take part in reactions, depletions in an element concentration only occur when it is sufficiently soluble in the fluid to be carried for long distances, either in the order of centimetres or metres, to be redeposited in vein systems which are not considered to be part of the rock, or over thousands of metres, to be removed completely from the area where the element was derived. In the case of the two elements, silicon and calcium, which have suffered major depletions, the calcium has probably been at least in part deposited in local calcite veins, although fluid inclusion data indicates that most of the large veins are in fact derived from outside the Pinbain lavas (chapter 7), while the silicon, and some of the calcium has been carried away from the succession.

Sodium, volatiles, and some potassium have been introduced to the succession. It has been proved by stable isotope studies (chapter 6) that considerable volumes of sea water have flowed through the Pinbain Block, and this is probably the source of these elements. Aluminium

has also been added to these rocks, but this is unlikely to have been derived from normal sea water, because this does not contain much aluminium. It is possible that the sea water was enriched in aluminium during its passage through the sediments overlying the Pinbain lavas, and subsequently redeposited the aluminium in the Pinbain Block.

Magnesium appears from its lack of correlation with the titanium and zirconium contents of the rocks to have been mobile, but shows no signs of overall depletion or enrichment. This element has probably been mobile within the succession, on a scale sufficient to destroy its original igneous distribution, i.e. it must have moved at least a metre or more, so as to pass from its original flow units into those with different degrees of fractionation. Iron correlates much better with zirconium and titanium, but shows a sufficient degree of scatter to suggest that it also may have been locally mobile.

#### 5.3.1.4.1 The HSG

The high silica group rocks must be discussed separately from the remainder of the Pinbain rocks because they do not lie on the same zirconium-titanium trend. They also show several variations in their major element chemistry. Foremost in this is their high silica and low magnesium content. These could have resulted from their being more fractionated, and thus would be an original igneous feature. They also have low manganese contents, which could be original. However, the iron and titanium contents vary considerably within the

group, and do not support their origin by fractionation, and since iron and titanium have been shown to be immobile in the other rocks, the high-silica group must have a more complex origin. It is likely that they have undergone a different set of alteration processes, which have resulted in titanium and/or zirconium becoming mobile. The difference in alteration may have resulted from local variations in the fluid composition. In particular, the mobility of titanium and zirconium may indicate the presence of carbon dioxide rich fluids, which Hynes (1980) has indicated can cause mobility in these elements.

#### 5.3.1.4.2 Volatile Content

The volatile content in the Pinbain rocks is much higher than in normal basalts, reflecting the growth of hydrous minerals such as chlorite, and also the presence of calcite, giving off the volatile carbon dioxide. The volatile content is partly controlled by the pre-existing rock composition, because as was shown above, the LTG, which contain little or no titanite tend to have higher volatile contents. The lack of pyroxene in the rocks means that there is a higher proportion of the other constituents, i.e. plagioclase and matrix, which was originally volcanic glass, or very finely crystalline material. Since most of the hydrous material in the altered rocks is chlorite, and this is found mainly in the matrix, the higher volatile content may be the result of more chlorite growth, simply because there was more space available for it. Alternatively, the extra plagioclase present in the rock may have caused the higher

volatile content by releasing calcium during albitisation, which was fixed in the rock as calcite, which contributes CO<sub>2</sub> to the loss on ignition. This is perhaps less likely, since it appears from the evidence discussed above that the calcium has largely been leached from the rocks. It is possible that both these processes operated simultaneously.

### 5.3.2 Trace Elements

#### 5.3.2.1 Fractionation

The only trace element which show a good correlation with zirconium, and can thus be considered to be immobile is yttrium (fig 5.18). Two elements show a less good, but still discernable correlation. These are niobium (fig 5.19) and copper (fig 5.20). In the case of these elements it is uncertain whether the variations from a good line are due to alteration or are original, related to changes in the original fractionation process.

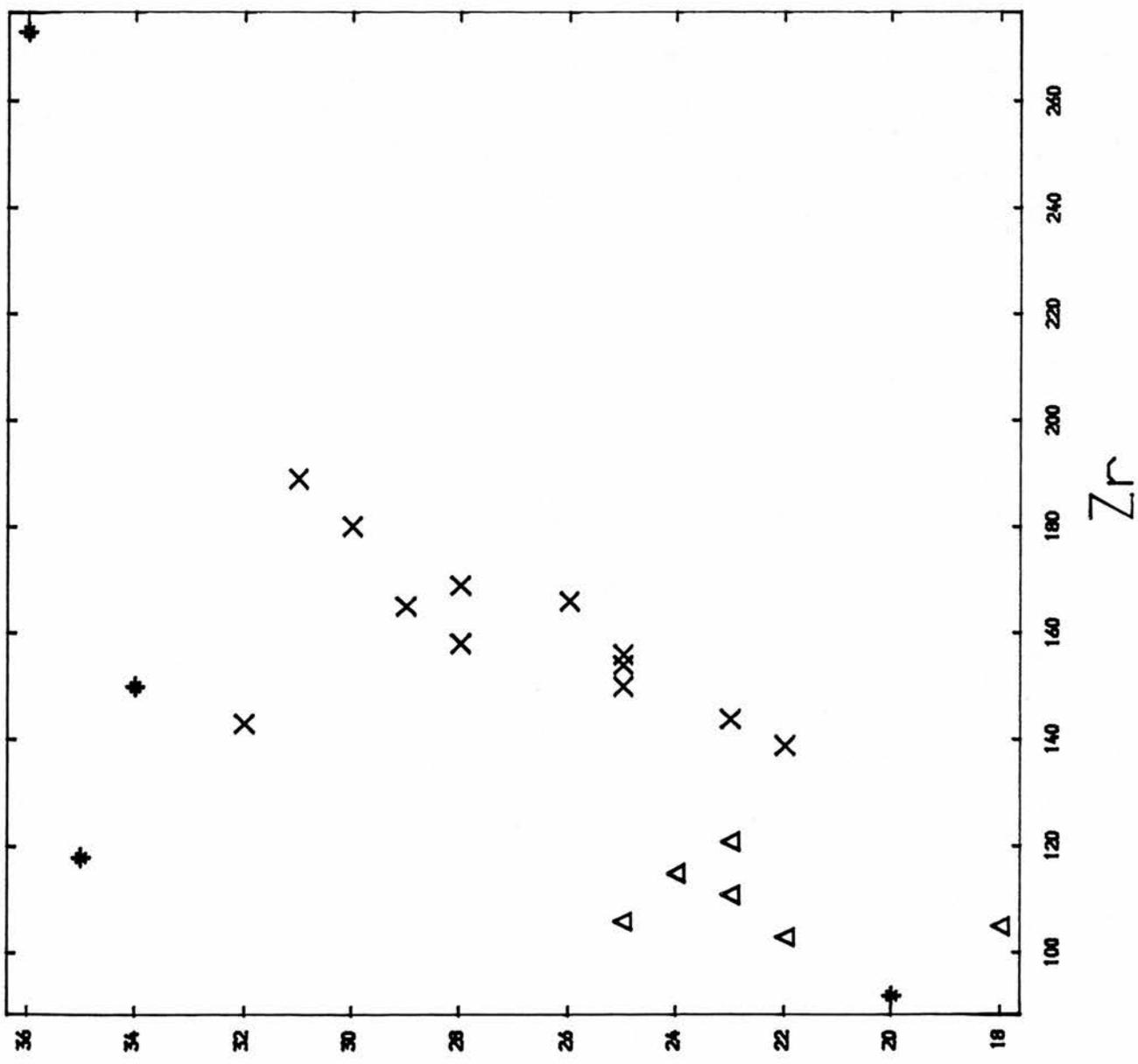
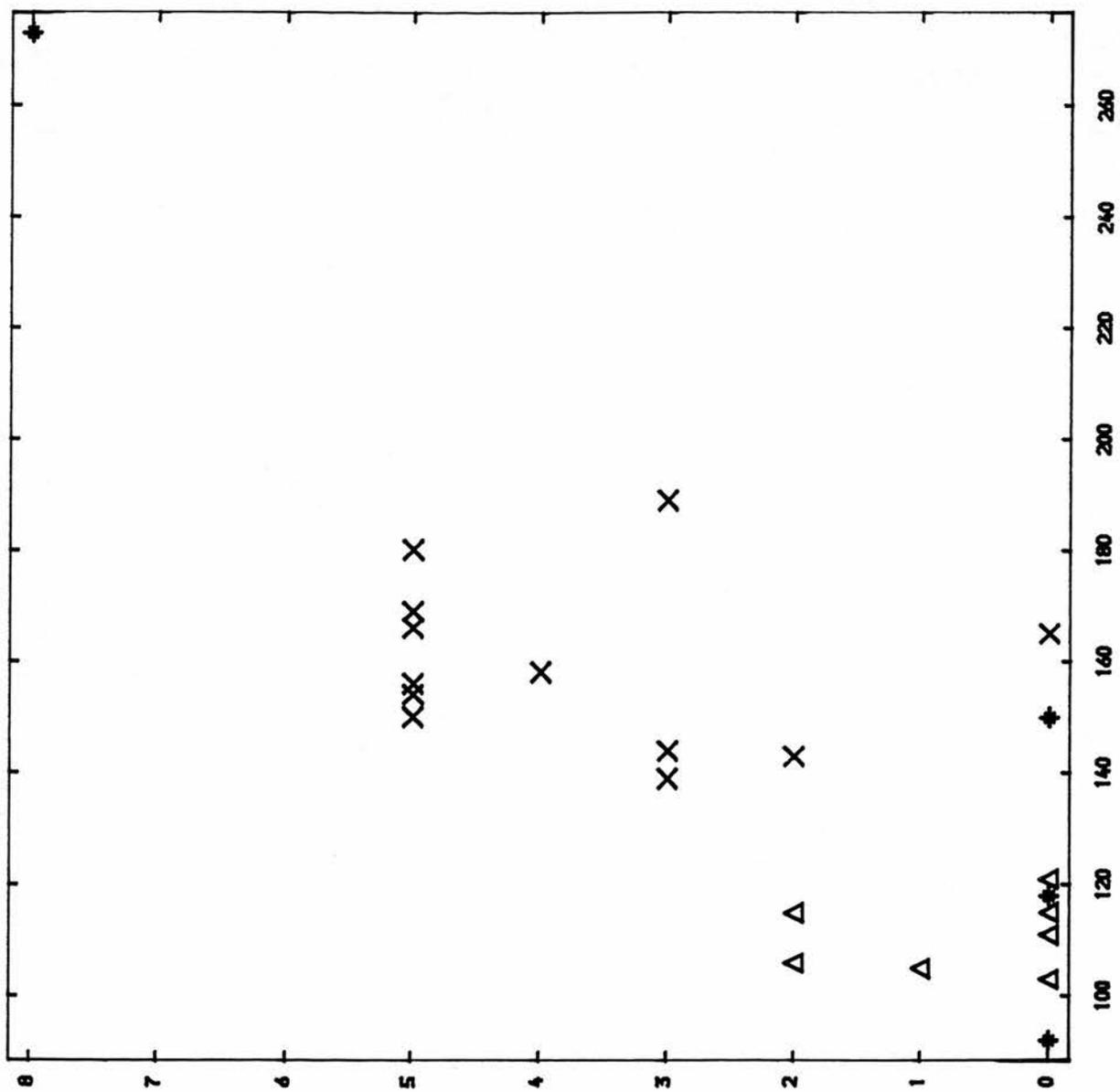


FIG 5:18

Y

Zr



Symbol	N	r	Group
◆	4	0.96	HSG
△	7	-0.20	LTG
X	12	0.13	HTG

FIG 5.19

Np

Zr

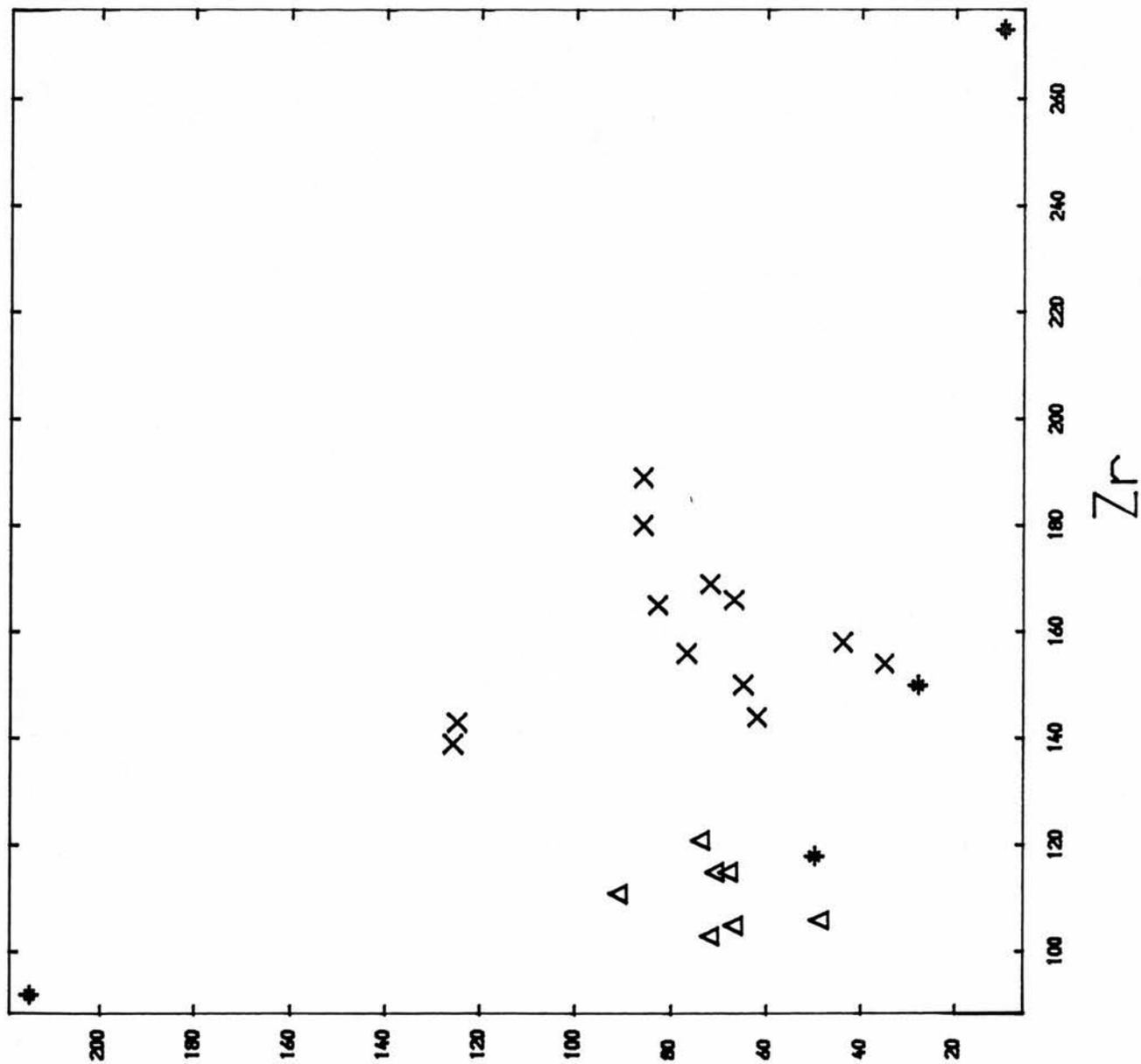


FIG 5.20

Symbol	N	r	Group
◆	4	-0.68	HSG
Δ	7	0.30	LTG
X	12	-0.18	HTG

### 5.3.2.2 Water Related Alteration

The concentration of trace elements was plotted against weight loss on ignition in order to determine if there were any correlations. If correlations do occur then the element can be considered to be mobile, with a simple relationship between the amount of water passing through the rock, if the assumptions discussed above (section 5.3) are correct.

Possible correlations between loss on ignition and concentration were observed for four elements. Niobium (fig 5.21) and cerium (fig 5.22) showed a negative correlation with volatile content, i.e. the element is progressively depleted as the water (and/or carbonate) content increased. Thorium also appeared to show this trend (fig 5.23), although very little thorium is actually present in these rocks, and the trend may be spurious, depending on only one sample with high thorium. The evidence for the mobility of niobium is contradictory to the previous section, where it was suggested that niobium is in fact immobile. This will be discussed below (section 5.3.2.3.3).

Nickel differs from the elements discussed above in that it shows a weak positive correlation with loss on ignition (fig 5.24), which should indicate that it has been enriched as more water has passed through the rock. In the next section (5.3.2.3) however, contradictory evidence suggests that nickel has actually been depleted.

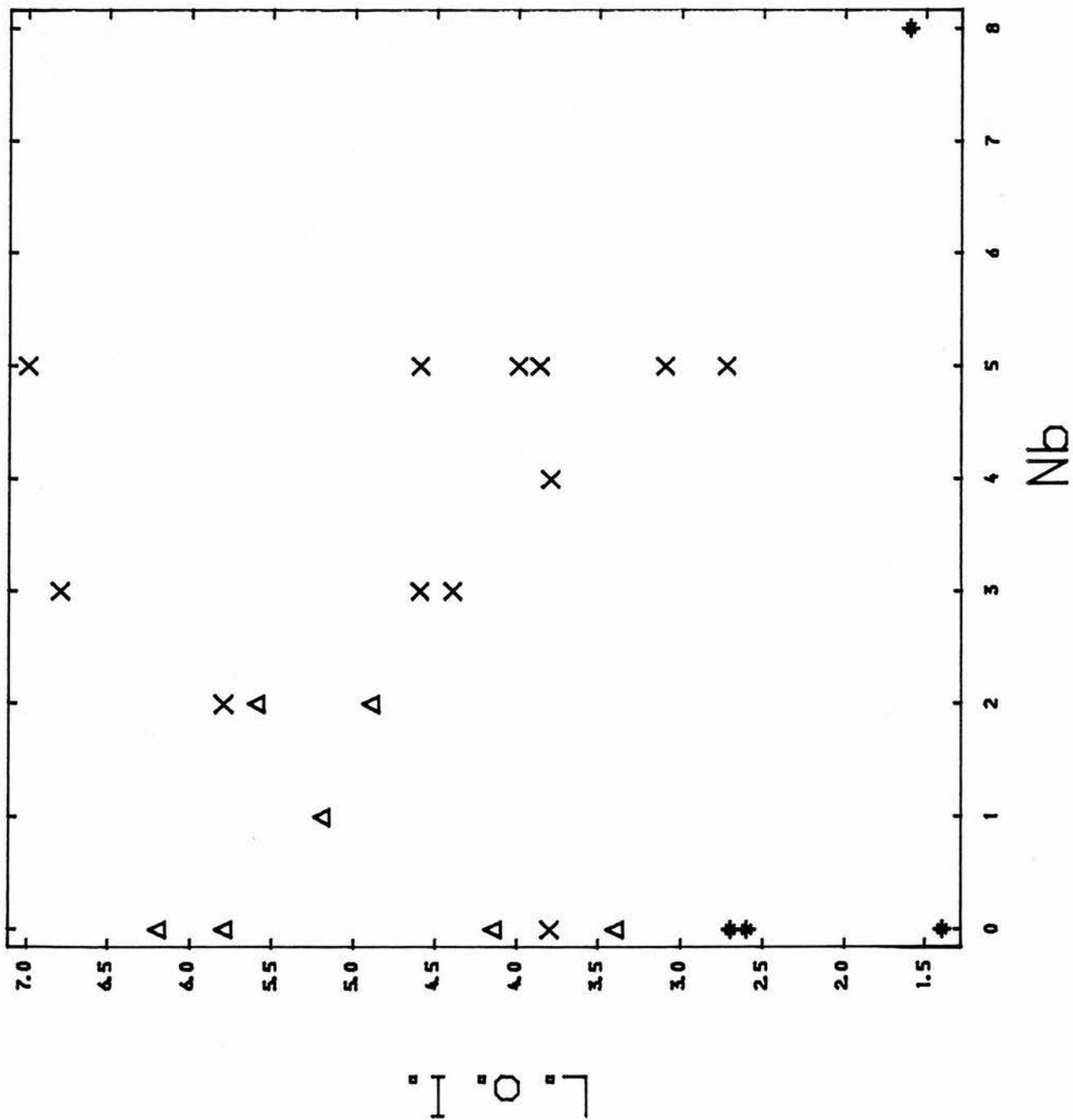
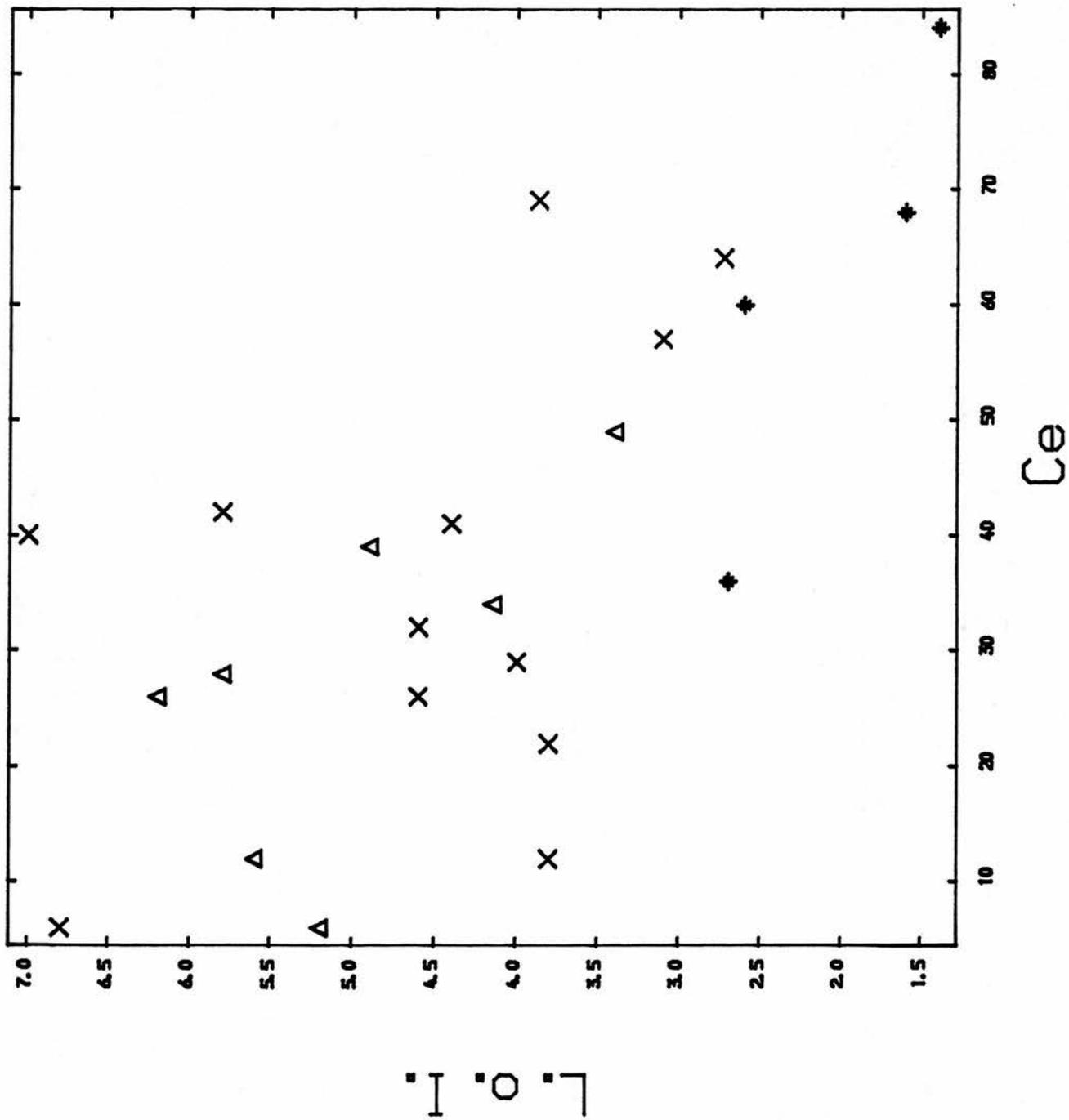
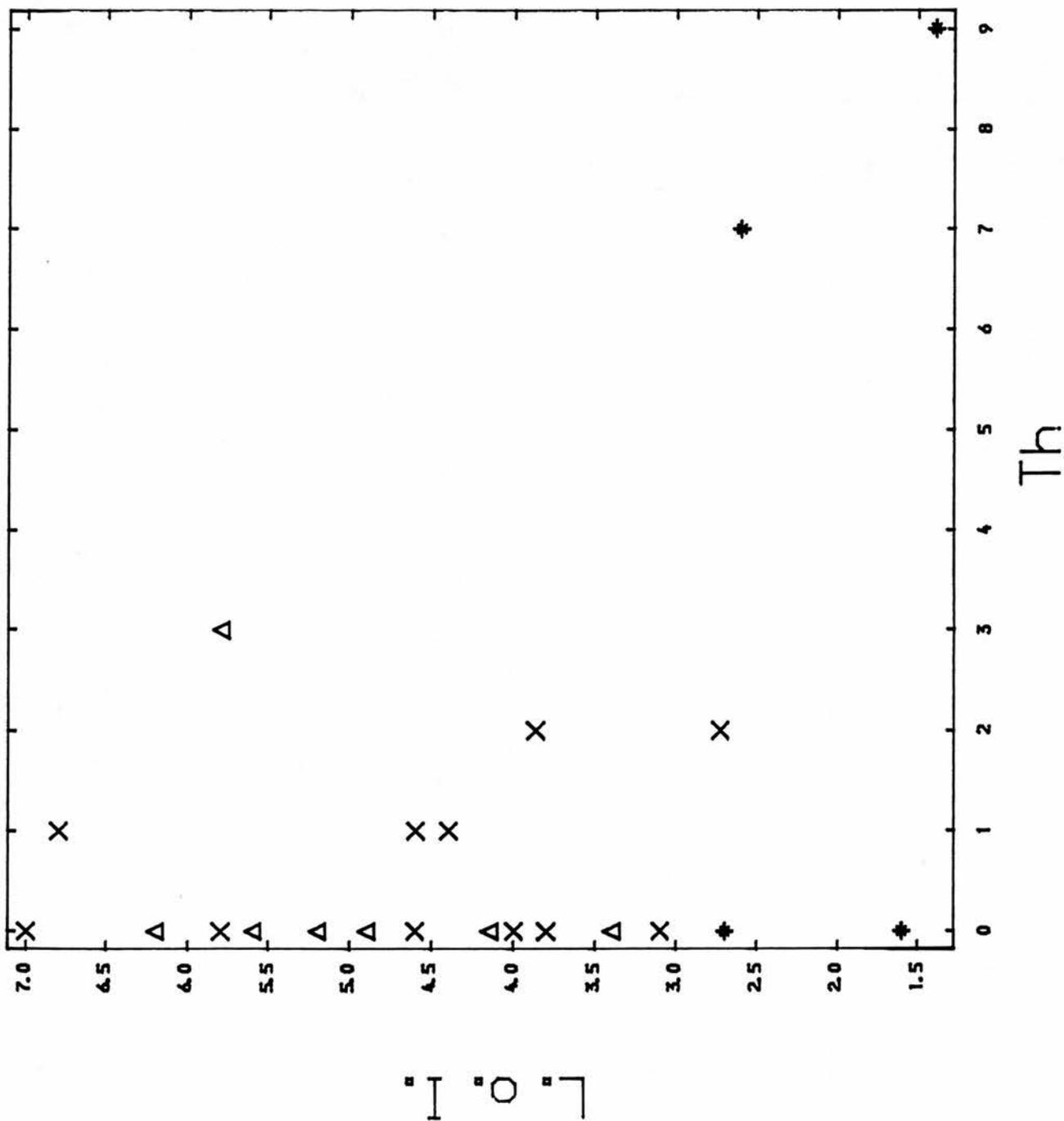


FIG 5.21



Symbol	N	r	Group
◆	4	-0.87	HSG
△	7	-0.64	LTG
X	12	-0.42	HTG

FIG 5.22



Symbol	N	r	Group
◆	4	-0.25	HSG
△	7	0.34	LTG
×	12	-0.24	HTG

FIG 5.23

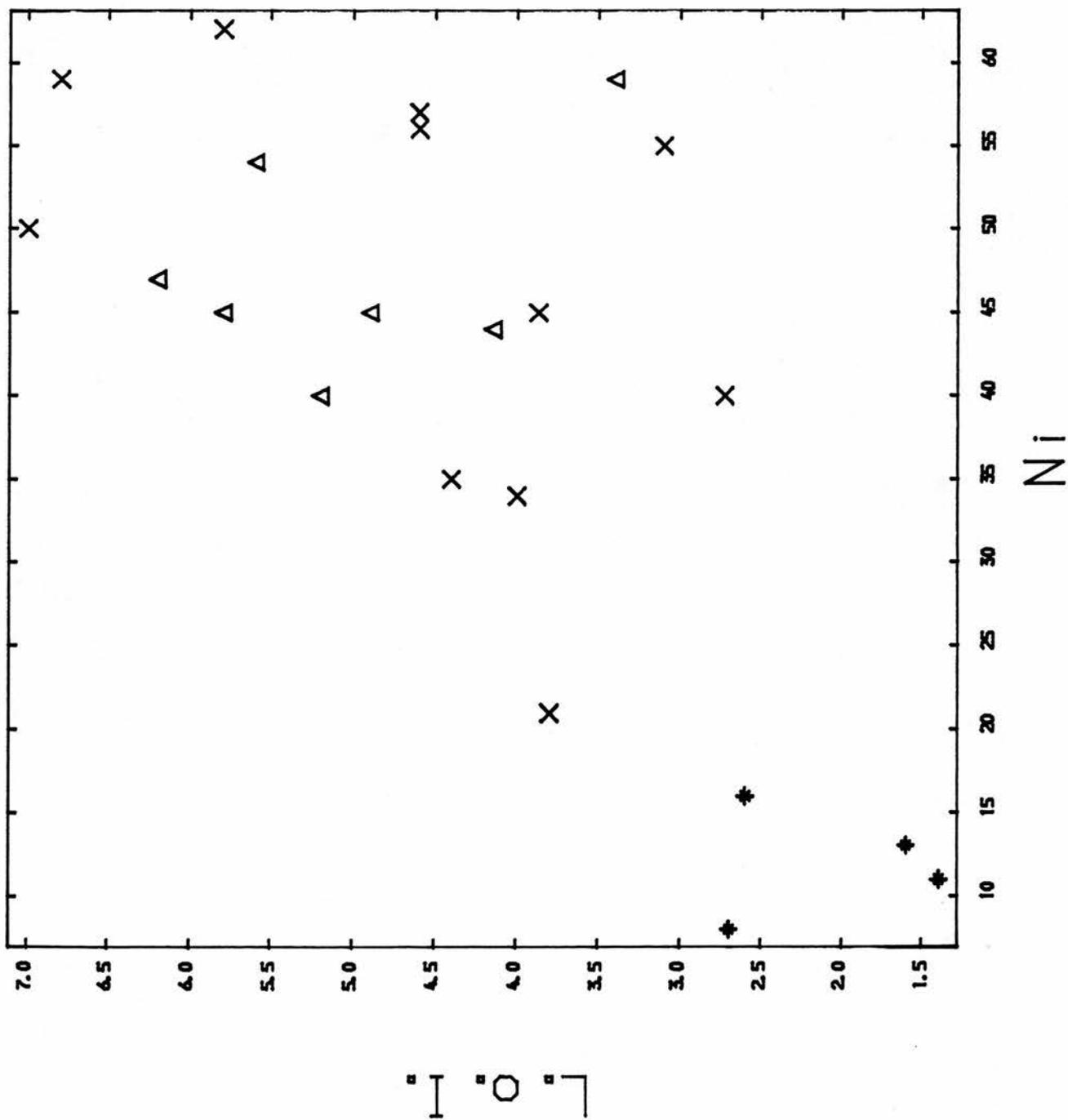


FIG 5.24

### 5.3.2.3 Comparison With Average Basalt

The lack of correlation with the concentration of volatiles in a rock does not necessarily mean that the element is immobile, merely that it is not simply related to the amount of water in the rock. By comparing the Pinbain lavas with normal basalts it is possible to estimate the chemical differences between them. These will be mainly due to alteration, since the composition of basalts is not subject to great variations. Mean trace element concentrations (in ppm) in normal basalts are given in the table below, along with averages and ranges for the Pinbain rocks. The average data are taken from Wedepohl (1978).

ELEMENT	AVERAGE	PINBAIN	RANGE
Nb	10.7	2.5	0-8
Zr	150-200	144.5	92-273
Y	30	26.4	18-36
Sr	329	295.3	60-592
Rb	8	11.4	4-29
Th	0.1-2	1.1	0-9
Pb	3-4	5.2	0-24
Zn	80-120	88.1	66-149
Cu	40-60	74.9	10-215
Ni	120/191	39.9	8-62
Cr	250	44.4	0-113
V	251	281.0	59-380
Ba	246	187.8	10-709
Hf	3-4	3.5	2-10
Ce	25	38.3	6-84
La	10	3.2	0-31

N.B. the averages are for ocean island tholeiites, if available, or for a given suite of ocean island tholeiites, usually from Hawaii, if not. The nickel averages are for world basalts/hawaiian basalts, respectively.

The figures given in the table above will be considered in conjunction with the histograms of trace element concentrations (fig 5.25). It is probable that when an element occurs in amounts comparable with normal basalts, and when its histogram shows a narrow compositional range, that that element has been immobile. The varying amount of alteration in these rocks, as evidenced by their varying water contents, and the variable preservation of original mineralogy, suggests that if an element is mobile then its concentration will vary widely, because of the varying amount of alteration.

#### 5.3.2.3.1 Largely Immobile Elements

Those elements which were used to identify the petrotectonic environment of the Pinbain lavas (section 5.2), i.e. zirconium and yttrium both show a narrow range of compositions, with the exception of one value for zirconium. The histograms both show a bimodal pattern, which probably reflects the two kinds of lava present in the succession, i.e. those with titanite and those without. Both zirconium and yttrium have concentrations which fall slightly below the normal values for ocean-island tholeiites, but the evidence for immobility shows that this must be due to petrological factors and not to alteration.

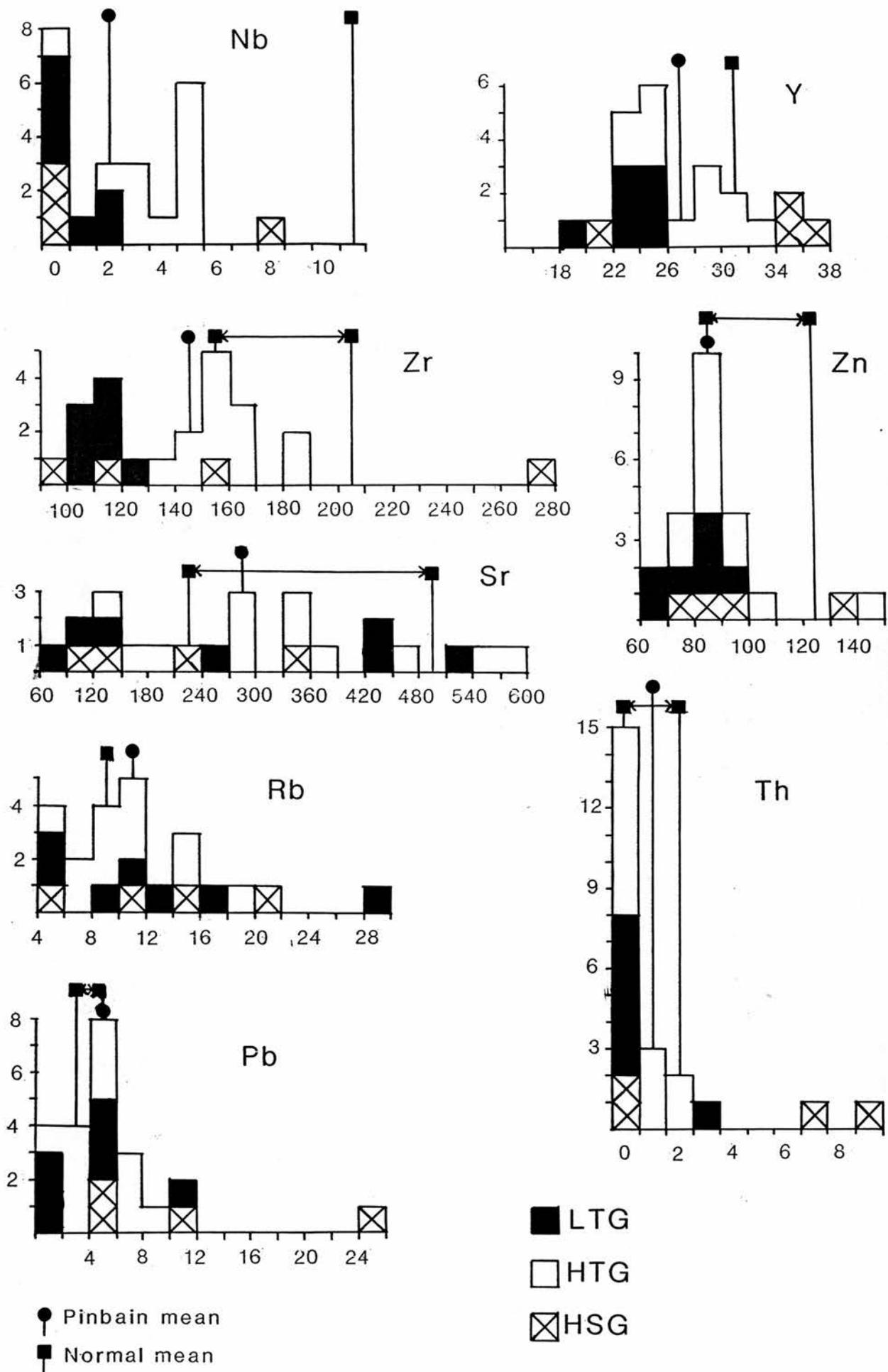


FIG 5.25. Histograms of trace element concentrations (ppm). Note that for Cr and Ni the normal mean plots off the histogram

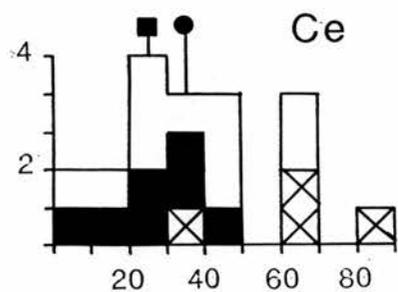
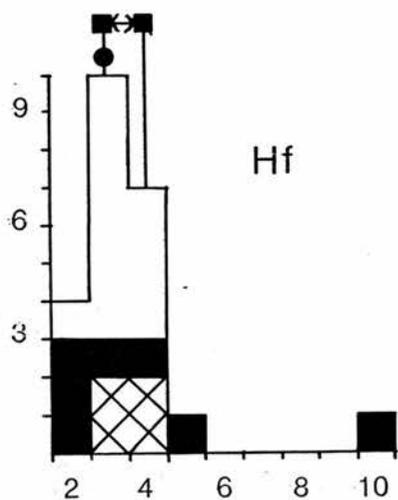
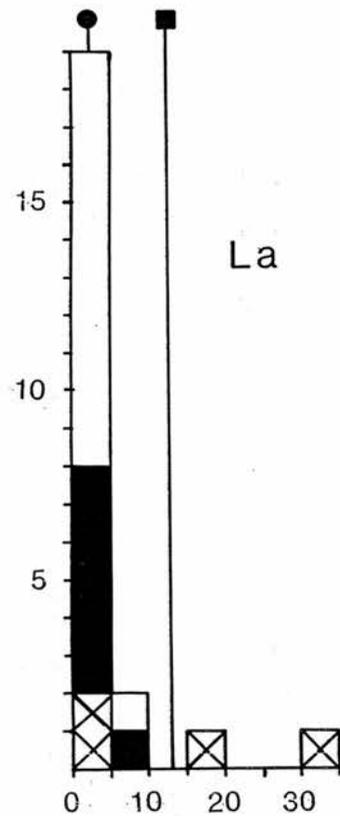
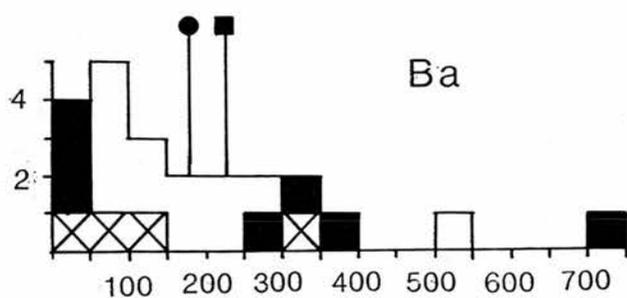
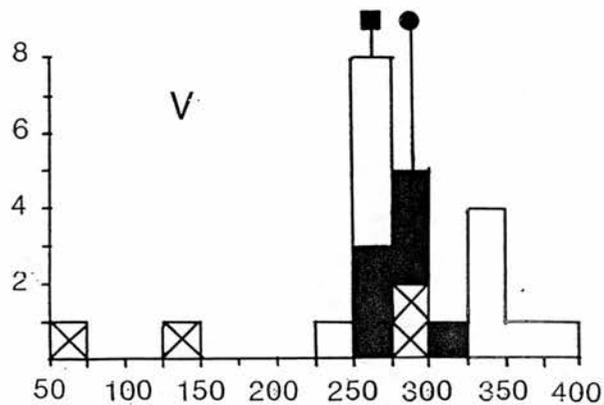
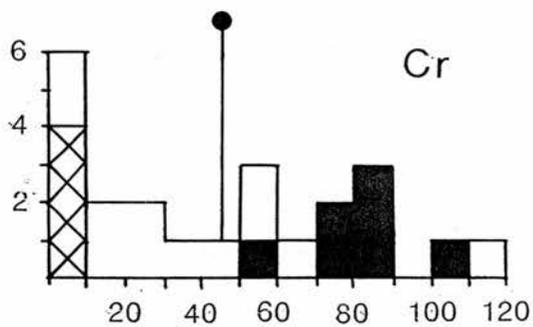
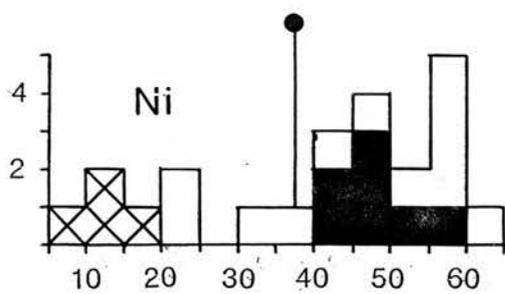
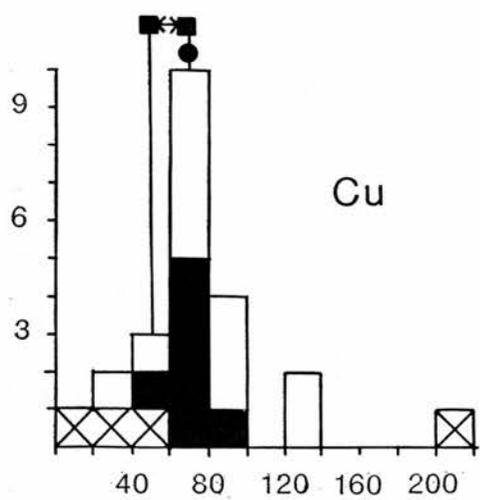


FIG 5.25. cont.

Rubidium is another element which appears to be largely immobile. The rubidium concentration in the Pinbain rocks is close to that for normal basalts, and the histogram is fairly well constrained. As in the case of zirconium, there is one anomalous value, although these come from different samples, and in addition there appears to be a slight tailing of the histogram towards the high concentration side. This may indicate that in some samples conditions became extreme enough to alter the rubidium content. This would be expected, since the chemistry of rubidium closely follows that of potassium, which has also occasionally been enriched in these rocks. The extra potassium and rubidium must be supplied from sea-water.

Thorium is probably immobile. The average for Pinbain is within the normal range for ocean-island tholeiites. There are two abnormal values, but these cannot be considered to be significant, particularly since there is a large degree of error in these very low concentrations.

The lead histogram shows a tight clustering of concentrations, with a limited range. The average is very similar to that for normal basalts, and therefore this evidence suggests that lead is immobile under these conditions. There is one anomalous value, as in the case of zirconium and rubidium, but again from a different sample.

Zinc shows a tight clustering of concentration values, and the average is within the range for unaltered basalts, and so it is probable that zinc has been immobile. Again, however, there are anomalous results.

Copper is also immobile. The histogram again shows a narrow range of values close to those for normal basalts.

Vanadium shows similar features to all the examples above, i.e. a tightly constrained histogram, and an average value close to that for unaltered basalts. Vanadium also has two anomalous values, but unlike the elements above the unusual values are low compared to the normal range. This will be discussed in section 5.3.2.3.2 below.

Hafnium has almost certainly been immobile, as can be seen from the histogram, and from comparison of the average with that for normal basalts. There is one unusually high value.

Cerium is the final element which this data suggests has been immobile. The histogram is tightly constrained, and the average is very similar to that which would be expected in a fresh basalt.

#### 5.3.2.3.2 Anomalous Values For Otherwise Immobile Trace Elements

Most of the elements discussed above show a narrow range of concentration in general, but with one or two anomalous values, which come from different samples for different elements. In the case of rubidium there is also a tailing of the histogram, and this, together, with related evidence for the behaviour of potassium suggests that in some of the samples rubidium has been enriched by interaction with sea-water.

Vanadium shows two anomalous values, which are lower than the average. This suggests that vanadium has been leached out of the rock under extreme conditions, although it is generally immobile. The conditions required to mobilise it are not known, but are presumably not related only to the amount of water passing through, since there are only two samples in which it is mobilised, and there is no correlation with water content (fig 5.26).

The other elements, Zr, Th, Pb, Zn, Cu, Hf, and possibly Ce all show one or two values which are much higher than the rest. These are difficult to account for. They come from different samples, and so it is probably not instrumental error. A certain variation in the concentration of these elements would normally be expected, but not in one direction only - there should be low values as well as high. There is a possibility that, purely by chance, a sample selected for analysis could contain a mineral with a high concentration of the element concerned - especially when in trace concentration, the presence of one grain could contaminate the whole sample. If the

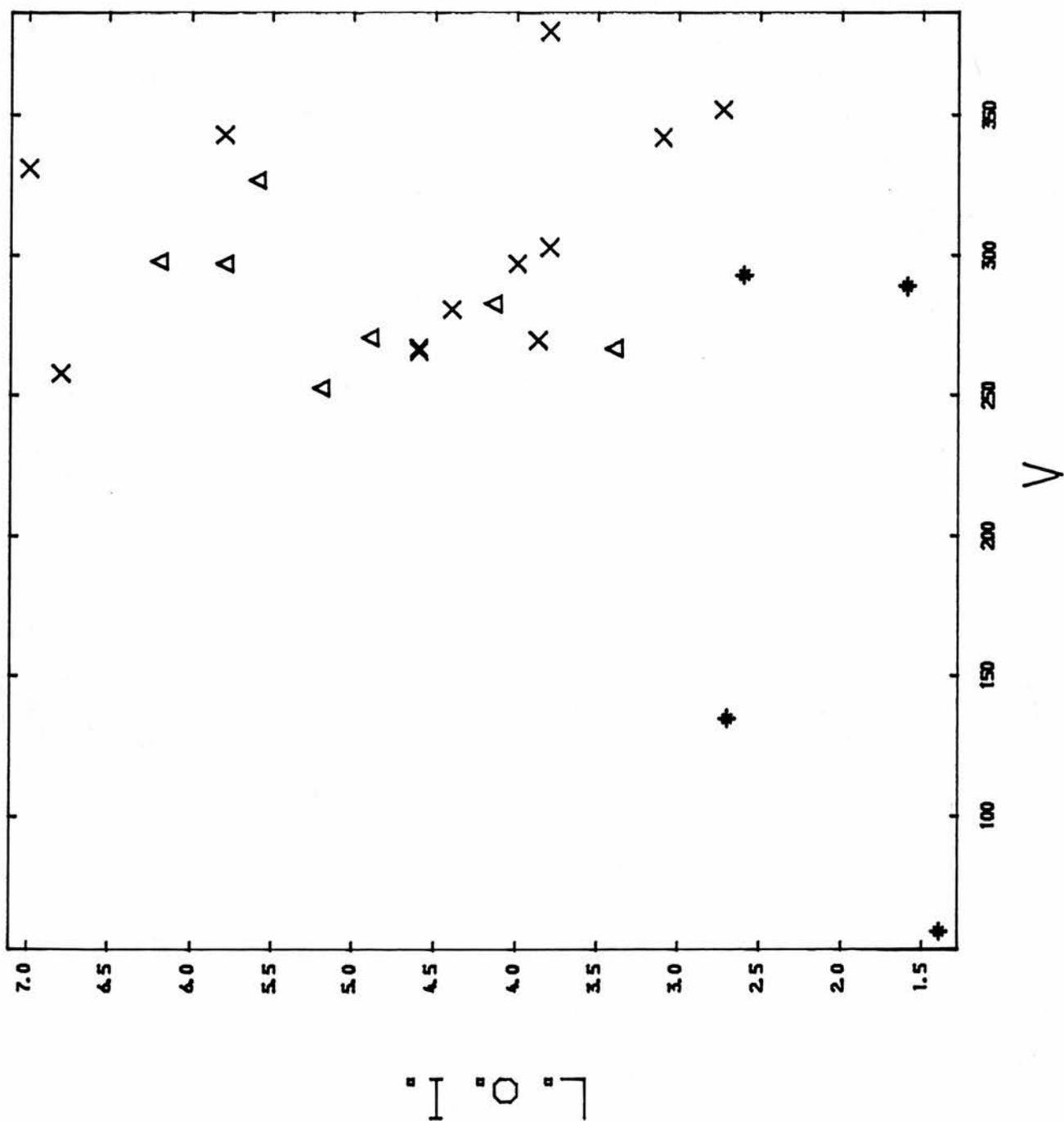


FIG 5.26

mineral was so rare in these rocks that the other samples contained none of it, then an anomalous value would result. Of course, there would have to be several different minerals, because the anomalies occur in different rocks for different elements.

An alternative explanation for the anomalies is that under some conditions the element is enriched in these rocks during alteration. This seems likely in the case of rubidium, as explained above, but it is improbable for the other elements because sea-water contains very little of them, and also because, unlike the histogram for rubidium, which shows a tail towards the high side, it is an all or nothing process - there is no evidence for a variable degree of enrichment, only one or two values which are completely separate from the others.

#### 5.3.2.3.3 Mobile Trace Elements

Element mobility in the Pinbain rocks can be demonstrated by this method for several elements. One of these is barium, an element which has been shown experimentally to be extremely mobile (Mottl & Holland 1978). A barium content of 2-300 ppm is normal for basaltic rocks (Wedepohl 1978). The barium content for the Pinbain rocks varies between 10 and 709 ppm, so it is likely that barium has been extremely mobile in these rocks. The histogram shows, that although the average for the Pinbain rocks is similar to that for normal basalts, there is a wide range, with most values being considerably depleted in barium relative to normal basalts. A few high values also occur. It is probable that in general, barium has been leached out of the Pinbain

rocks during alteration. Mottl & Holland (1978) showed experimentally that barium is leached out of basalts by sea water. The few samples showing enrichment probably derive barium from other rocks in the succession, with some special factor causing it to become concentrated, probably in the feldspars.

Strontium shows a similar pattern to barium. The range of concentration is very wide, extending well beyond the range for normal basalt, and with such a spread that the average means very little. The original composition was probably very similar to that of normal ocean-island tholeiites, as shown by the small hump in the centre of the histogram. The majority of samples appear to have been depleted in strontium, although some are enriched. This indicates that strontium is mobile, but is redistributed within the system, as well as being removed altogether.

The final elements to be considered are nickel, chromium, niobium and lanthanum. These all have concentrations considerably lower than equivalent normal basalts. The nickel and chromium also have a fairly broad histogram, without well-defined peaks. Niobium has been considerably depleted, while lanthanum appears to have been almost completely removed from these rocks, with the exception of one rock which has a reasonably normal composition, and one which appears to have been enriched.

The nickel concentration is considerably depleted relative to normal basalts. This contradicts the evidence for enrichment which is given above (section 5.3.2.2), where it was shown that the nickel concentration is positively correlated with volatile content. The depletion is so marked, however, that the enrichment trend must be spurious.

#### 5.3.2.4 Trace Element Conclusions

These studies enable the degree of mobility of most of these elements to be determined. Only yttrium correlates well with zirconium, and from this and from its comparison with normal basalts it can be considered to be immobile. Niobium and copper show slight traces of correlation with zirconium. The rest of the elements show no correlation. This may be because there was no correlation prior to alteration, or it may be that most of the elements have shown limited mobility, which has destroyed their correlation with zirconium, without changing their overall concentration. The comparison with normal basalts shows that thorium, zinc, copper, vanadium, hafnium and cerium are all present in well-constrained histograms, with concentrations similar to normal basalts, and thus they are considered to be largely immobile, despite their lack of correlation with zirconium. Rubidium generally falls into this group, although some of the samples do show rubidium enrichment.

Those elements which appear to be mobile are barium and strontium, both of which are usually depleted, although some samples show enrichment, and nickel, chromium, niobium and lanthanum which are all depleted. Niobium shows slight traces of a correlation with zirconium, but the concentration of niobium in these rocks is well below normal basalt values.

The technique of plotting element concentration against loss on ignition does not appear to be useful in these rocks. Only niobium showed a realistic trend of depletion with increasing volatiles, and also showed overall depletion relative to normal basalts. Cerium and thorium showed a similar trend against loss, but they have normal igneous concentrations. Nickel showed a positive correlation against loss, but it is considerably depleted relative to normal basalt. The volatile content of these rocks is partly controlled by the composition, as discussed in the major element section, and this may have prevented correlations developing, since the volatile content is not a simple function of the degree of alteration. Those correlations which do exist between elements and loss may be the remnant of an original igneous variation between the pyroxene and non-pyroxene rocks.

Both nickel and niobium have been generally considered to be immobile elements (e.g. Pearce & Cann 1973; Marsh et al. 1980; Thirlwall & Bluck 1984), but the evidence for depletion of these elements in the Pinbain rocks casts doubts on this. The concentration of nickel varies from 8 to 50 ppm, and that of niobium from 0 to 8

ppm. Niobium has in many cases been almost completely removed from the rock, although its initial concentration was probably not very high, probably around the 10 to 20 ppm recorded by Holub et al. (1984) in relatively fresh dykes which are similar to the original Pinbain basalts. Niobium appears to retain a correlation with zirconium, but there are a lot of zero analyses, and the correlation may be fortuitous. Caution must be applied when using these elements for discrimination between environments.

The extraction of elements by percolating water can be explained simply by dissolution - the element concerned being sufficiently soluble to dissolve as it is released from minerals by chemical reactions during alteration. The passage of more water results in more alteration, greater depletion of the elements concerned, and a higher loss on ignition in the analysis. However, the relationship is not simple, because only niobium seems to give a trend of depletion with increasing LOI, which is consistent with its actual depletion relative to normal basalt. For the other apparent correlations between LOI and elements, the enrichment of nickel with increasing alteration is impossible, because the rocks are actually highly depleted in nickel. Cerium appears to have a depletion trend, but this does not appear in its histogram, which shows that it is probably unaltered.

### 5.3.3 Discussion

The final part of this chapter is a comparison between the chemical changes in the Pinbain rocks, and those observed in similar successions from other parts of the world. This will show whether or not similar processes have operated, or whether the Pinbain succession shows any peculiarities.

That elements can be locally redistributed within a rock has been shown by Nicholls (1959). He found that in spilites from the Built volcanic series there are highly altered 'sacs' in the rock where silicon, aluminium, calcium, magnesium and iron become concentrated, while sodium is enriched elsewhere in the rock. In the altered sacs the plagioclase is completely broken down to pumpellyite, and other alteration products. As these areas may weather more than the rest of the rock, they could well be discarded prior to analysis, thus giving a false composition for the whole rock. In the Pinbain rocks all the feldspar has been retained, but it is still possible that such locally metasomatised areas can occur, and therefore signs of element depletion within the bulk of the succession do not necessarily imply that the element has been carried completely out of the succession.

Stern and Elthon (1979) have studied chemical changes in the Chilean ophiolites. They found that titanium, zirconium, yttrium and phosphorus are immobile, which agrees with the results found for Pinbain. Of the major elements they discovered that iron and magnesium are generally immobile, although highly recrystallized greenschists tend to lose magnesium. In the Pinbain block magnesium

appears to be mobile at a lower grade, but the iron is mainly immobile, as in Chile. In Chile, calcium is depleted and sodium enriched, as at Pinbain. Potassium and rubidium are enriched in the pillow lavas, which is the trend found at Pinbain in the samples where there has been any mobility in these elements. The only real difference in the major element chemistry between the two areas are that in Chile silica has been added to the rocks, whereas in the Pinbain rocks it appears to have been depleted. Apart from the trace elements that are immobile in both areas, Stern and Elthon found that the rare earth elements were immobile. In the Pinbain rocks it appears that cerium is mobile, while lanthanum cannot be proved to be immobile. This is another difference between the areas.

Mevel (1981) studied pumpellyite-bearing hydrothermally altered basalts from the Vema fracture zone of the mid-Atlantic ridge. She found that certain elements showed a correlation with the water content of the rock, which showed that silicon and calcium were depleted with increasing alteration. While the method of comparing element concentration to the volatile concentration did not work very well for the Pinbain rocks, the depletion of silicon and calcium is the same for both studies. However, in the Vema ridge rocks iron and magnesium were enriched, whereas in the Pinbain rocks iron was immobile and magnesium may have been depleted. Sodium was enriched in both studies.

Cann (1969) found that in spilites from the Carlsberg ridge, that calcium and aluminium have been depleted, and silicon, iron and sodium added. These results differ from the Pinbain results in that aluminium has been added to and silicon removed from the Pinbain rocks, while iron was immobile.

Walsh (1983) has looked at the mobility of trace elements in the Storen greenstones in Norway. He found that titanium, hafnium, scandium, phosphorus and the REE can all be mobilised by a carbon dioxide rich fluid. In the Pinbain rocks titanium and hafnium are immobile, although the REE seem to be mobile. This suggests that the fluids were not particularly rich in carbon dioxide. This conclusion is supported by the extensive occurrence of sphene in the Pinbain rocks (chapter 2), because sphene is not stable with a carbon dioxide rich fluid phase (Schuiling & Vink 1967).

Some experimental work has also been done on the alteration of basalts. For instance, Mottl & Holland (1978) discovered that magnesium and sodium are both added to basalts from sea-water. While the result for sodium agrees with evidence from Pinbain, and indeed from all spilites, it was found that for the Pinbain rocks magnesium was if anything leached out, rather than enriched. Mottl & Holland did however find that silica was leached out from the rocks, along with calcium, which agrees with the trends found in the Pinbain rocks. In the experimental system it was found that potassium was leached out, which does not occur at Pinbain. These experiments were carried out at relatively high temperature. At lower temperatures

<sup>o</sup>  
( $<250$  C) potassium is added to the basalts (Donnelly et al. 1979). The experimental leaching of barium is consistent with most of the Pinbain rocks, although some show an enrichment. Strontium appeared to be either enriched or depleted in the experiment, depending on the new phases growing. This seems to have occurred in the Pinbain rocks as well, with strontium being mobile, but being enriched and depleted in different samples.

Seyfried et al. (1978) experimentally altered basaltic glass with varying sea water-rock ratios, in order to determine the nature of alteration. They found that at  $350$  C, and a water/rock ratio of  $10$  sodium, magnesium and water are added to the rock, while calcium, silicon and potassium are lost. These changes are similar to those found in the Pinbain rocks, with the exception of potassium and magnesium. At water/rock ratios of  $60$  almost all of the calcium, sodium and potassium are leached out of the rock, along with some silicon. Magnesium and water are gained. Although the temperature in the experiment is different from that in the Pinbain block, these results suggest a constraint on the water/rock ratio for the Pinbain block, i.e. it must be less than  $60$ , and is more likely to be round about  $10$ . Since the stable isotope ratios are all in equilibrium for a water dominated system (chapter 6), the water/rock ratios must be over  $1$ .

This discussion shows that there is a considerable degree of comparability between the Pinbain rocks and other spilitic sequences around the world. Experimental evidence shows that the alteration is caused by an interaction with sea-water flowing through the rock.

Since the compositions of sea water and of basalts throughout the world are similar, it is not surprising that the resultant chemical changes are also similar. The Pinbain rocks show two major differences from other areas. The first is that the histogram for magnesium and the magnesium-zirconium diagram suggest that magnesium has been leached out of the Pinbain rocks, whereas experimental data, and evidence from other parts of the world suggest that magnesium is normally added to the rocks, until greenschist facies conditions are reached. The second difference between the Pinbain rocks and other areas is that aluminium has probably been added to the Pinbain sequence, whereas in other areas it has generally been immobile. The evidence for magnesium depletion in the Pinbain rocks is not particularly strong, and it may be that the magnesium was in fact enriched, and that the apparent depletion on the diagrams is spurious. The degree of scatter certainly shows that magnesium was mobile. An alternative explanation is that the water flowing through the Pinbain lavas may have had to pass through 3 or more kilometres of sediment before it reached the lavas. It may have been modified during this passage, and therefore have been unable to add magnesium to the rocks. This may also explain the addition of aluminium to the Pinbain rocks. The experimental studies used unmodified sea-water interacting with hot basalts, while most of the rock sequences studied underwent ocean-floor metamorphism under high geothermal gradients, and with little or no sedimentary cover, and are thus not directly comparable.

It must be emphasised that any modification of the sea-water can only be of a minor character, since its stable isotope ratios have not been affected (chapter 6), and most of the chemical changes in the Pinbain rocks are similar to those from elsewhere.

CHAPTER SIX

STABLE ISOTOPES

6.1 PURPOSE OF THE STUDY

Oxygen and hydrogen stable isotope studies were undertaken in order to determine the origin of the fluid phase present during the metamorphism of the Pinbain basalts. The possible source waters for the alteration are of three types :-

i) Ocean water

ii) Primary magmatic water (i.e. mantle or lower-crustal derived waters carried with the magma during its ascent).

iii) Meteoric water (water derived from precipitation moving downwards into the crust.

In addition, of course, there may be hybrid waters produced by a mixing of two or all of the primary waters.

If the water can be characterised then the fractionation between water and the rock can be used to provide an estimate of the temperature of equilibration. For reasons which will be explained in the relevant sections, in this study hydrogen isotope data was used to identify the water, while oxygen isotope data supplied thermometric

information.

## 6.2 METHODS AND NOTATION

### 6.2.1 Methods

For both hydrogen and oxygen isotope studies lava samples were chosen that were free from recent weathering. The samples were crushed to approximately 200 mesh size. Large veins were removed as far as possible, but veining and pore-fill is so extensive in these rocks that it was impossible to remove all vein material.

### 6.2.2 Hydrogen

Water was extracted from the samples by heating dried powders in platinum crucibles to approximately 1100°C, using a radio-frequency induction coil. Carbon dioxide was removed by freezing the water in an acetone-dry ice ("slush") trap, and the water was then de-oxygenated by hot uranium. The deuterium-hydrogen ratios were then determined relative to a local standard by a Micromass 602 mass spectrometer. Raw  $\delta$  values were then recalculated relative to SMOW, using the known ratio between the local standard and SMOW. The precision of the data is +/- 2.5%, and analysis of the NBS 30 standard gives a value of -65‰ (relative to SMOW) (A. Fallick, pers. comm.).

### 6.2.3 Oxygen

Oxygen was extracted from the powdered samples by heating them with chlorine trifluoride for twelve hours at 600°C. Free oxygen was then used to oxidise carbon electrodes to produce carbon dioxide. This method is detailed by Clayton & Mayeda (1963). The carbon dioxide samples were analysed on a Micromass 903 mass spectrometer against a local standard, with the results then being recalculated relative to SMOW. The precision of the data is +/- 0.25%, and the equipment gives a value of 9.6‰ (relative to SMOW) for the NBS 28 standard (A. Fallick, pers. comm.).

### 6.2.4 Notation

Isotope ratios are reported as  $\delta$  values, i.e. as the difference in parts per thousand, between the sample ratio and a standard ratio. Thus, for deuterium, D, and hydrogen, H, :-

$$\delta \frac{D}{H}_{\text{sample}} = \left[ \frac{D/H_{\text{sample}} - D/H_{\text{standard}}}{D/H_{\text{standard}}} \right] \times 10^3$$

The  $\delta$  value for oxygen is analogous, with the heavier isotope ( $^{18}\text{O}$ ) being the numerator, by convention.

This method of calculating isotope ratios means that it is not necessary to measure absolute ratios, which are far more difficult to determine than relative differences between ratios. Laboratories use internal standards when running samples, but to allow comparison with other work the  $\delta$  values are recalculated to be relative to an

international standard, which has been measured against the internal standard. The standard used for oxygen and hydrogen isotopes is SMOW, standard mean ocean water.

When a mineral phase is in equilibrium with a coexisting fluid there is an isotopic fractionation between the phases. The fractionation factor is known as  $\alpha$ , and is defined thus :-

$$\alpha_{\text{min-H}_2\text{O}} = \frac{R_{\text{min}}}{R_{\text{H}_2\text{O}}}$$

where min=mineral, and R represents an isotope ratio. Fractionation factors are related to temperature in the following manner :-

$$\Delta_{\text{min-H}_2\text{O}} = 1000 \ln \alpha_{\text{min-H}_2\text{O}} = A (10^6/T_K^2) - B$$

where the constants A and B are different for different minerals. These fractionation relationships will be discussed further for each isotope system below.

### 6.3 HYDROGEN ISOTOPES

#### 6.3.1 Results

The measured  $\delta$  deuterium values, relative to SMOW, are given in the table below:-

<u>SAMPLE</u>	<u>DELTA H (PER MIL)</u>
P14A	-69.41
P16	-53.87
P21	-61.09
S1	-54.77
S2	-51.48
S4	-66.99
S10	-61.23
S15	-60.76
P24	-65.36
P26	-64.24
P30	-71.38
P32	-54.61
P38	-55.66
P40	-57.81

These data are presented in fig 6.1.

### 6.3.2 Discussion

Basaltic rocks are essentially anhydrous when fresh - there are no hydrous phases present. This means that the hydrogen isotope composition of altered basalts is dependant only on the isotopic composition of the altering fluid, and the relevant fractionation factors. This means that the provenance of the fluid can be determined using hydrogen isotope data.

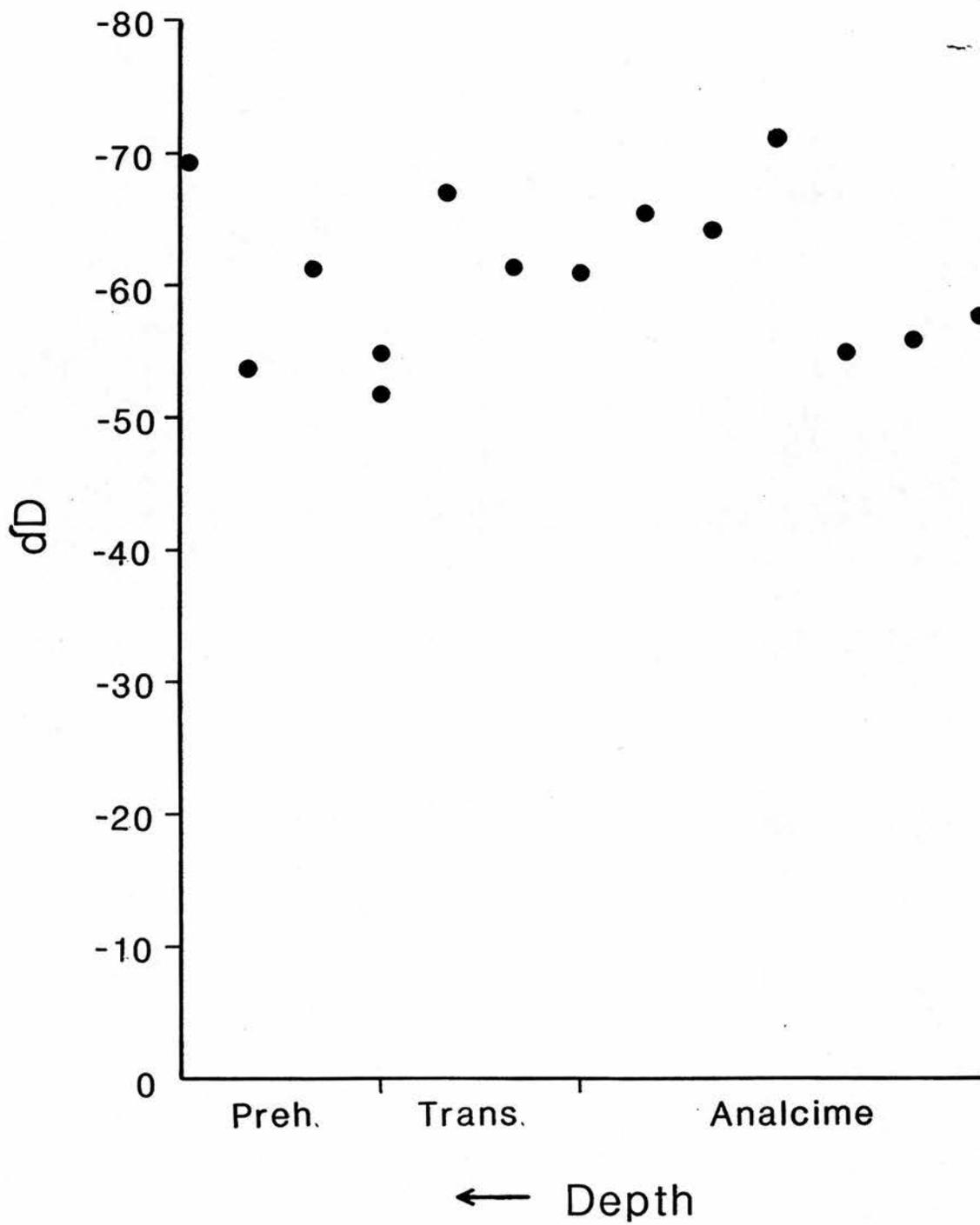


FIG 6.1. Hydrogen isotope ratios (relative to SMOW) for the Pinbain Block.

As can be seen from fig 6.1, the  $\delta D$  values range from -51.48 to -71.38‰. At temperatures from about 170°C upwards isotopic fractionation factors between minerals and water are almost independent of temperature, and range between -40 and -70‰ (Graham et al. 1980; Suzuki & Epstein 1976). From this data it can be seen that the fluid in equilibrium with the Pinbain rocks at the metamorphic temperature of about 190°C (chapter 8), or at higher temperatures, would have an isotopic composition within the limits of +19 to -30‰. The exact composition cannot be determined because of uncertainty in the fractionation factors, and the variable mineralogy of the Pinbain rocks.

These calculated values of the fluid which altered the Pinbain lavas are sufficient to rule out the possibility that primary magmatic water was the dominant fluid, because magmatic fluids have  $\delta D$  values of -40 to -80‰ (Sheppard et al. 1969). If magmatic waters had caused the spilitisation then the  $\delta D$  values for these samples would have been less than -100‰.

This leaves ocean or meteoric water as the possible source of water for the metamorphism. It is now generally accepted that the deuterium and oxygen isotope ratios of sea water have remained more or less constant throughout the Phanerozoic (Muehlenbachs & Clayton 1976), i.e. both the  $\delta D$  and  $\delta^{18}O$  values would be 0 relative to SMOW, and there is no reason to assume that the meteorological processes producing meteoric water have changed. It is therefore justifiable to apply arguments used for recent systems to these ancient rocks.

The relationship between various waters are shown on fig 6.2. Meteoric fluids are derived from seawater by the processes of evaporation and precipitation. Meteoric waters from near the equator are very close to sea-water in isotopic composition. As atmospheric circulation carries water towards the poles there is an enrichment in light isotopes because the heavier isotope (deuterium) is quicker to condense, and light isotopes evaporate more rapidly when precipitation is re-evaporated.

Unfortunately, palaeomagnetic studies (Smith et al. 1981) have shown that from the end of the Ordovician to the Devonian the site of the Ballantrae Complex lay about  $10^{\circ}$  south of the equator. This means that meteoric and sea water compositions would have been very similar in isotopic composition, and the stable isotope method cannot be used to distinguish between them. This is particularly true for whole rock isotope values because uncertainty as to the exact mineral composition of the sample means that the fractionation factor used cannot be exactly determined, even assuming that fractionation data are available for all the minerals in the rock.

In the case of the Pinbain succession, however, the submarine character of the basalts and the presence of marine fossils in sediments in the lavas (Rushton et al. 1986) and in their sedimentary cover (Williams 1962), and the extensive albitisation which requires a sodium rich fluid all suggest that the fluid present during metamorphism was largely, or wholly derived from sea water.

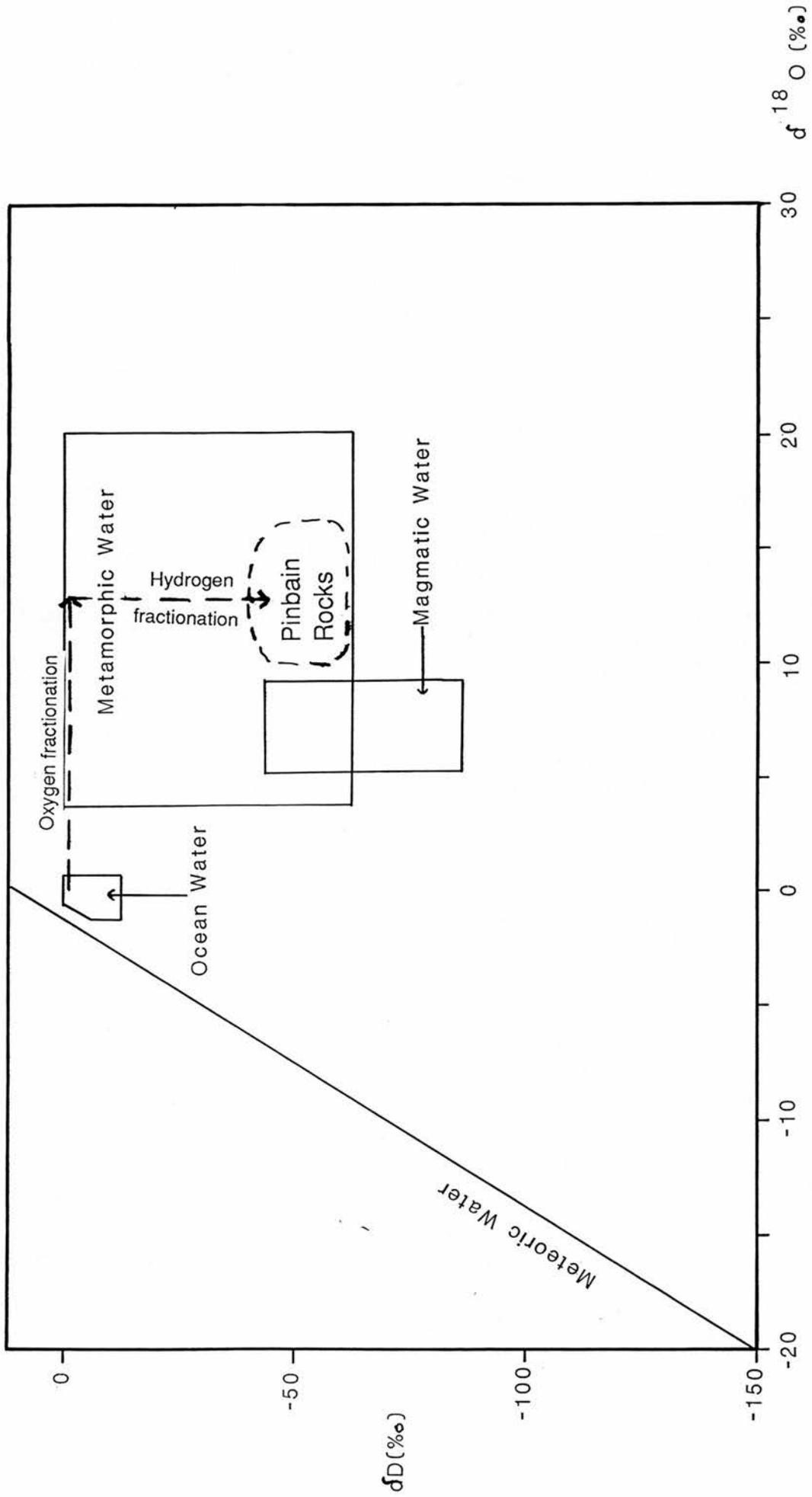


FIG 6.2. Hydrogen and oxygen isotope ratios (relative to SMOW) for natural waters.

### 6.3.3 Summary

The deuterium-hydrogen isotope data conclusively rule out any major contribution of magmatic water. They are consistent with either meteoric or sea water, but other considerations suggest that sea water was the dominant metamorphic fluid.

## 6.4 OXYGEN ISOTOPES

### 6.4.1 Results

$\delta^{18}\text{O}$  values relative to SMOW for rocks in the Pinbain block are given in the table below:-

<u>SAMPLE</u>	<u>MEAN DELTA</u>	<u><math>^{18}\text{O}</math></u>	
P14A	11.928	S15	12.327
P16	11.199	P24	10.727
P21	11.384	P26	11.290
S1	7.997	P30	9.788
S2	10.342	P32	11.304
S4	12.306	P35	12.148
S11	12.210	P35	12.148
S13	11.735	P40	15.362
P38	12.557		

#### 6.4.2 Temperature

These data, when plotted against depth (fig 6.3), show no real gradient over the 1200 m or so of vertical lava succession. Oxygen isotope fractionations are strongly temperature-dependant, so these data show that there was not a pronounced geothermal gradient at the time of alteration. As would be expected, the three topmost samples have the heaviest isotopic composition, i.e. the lowest temperature.

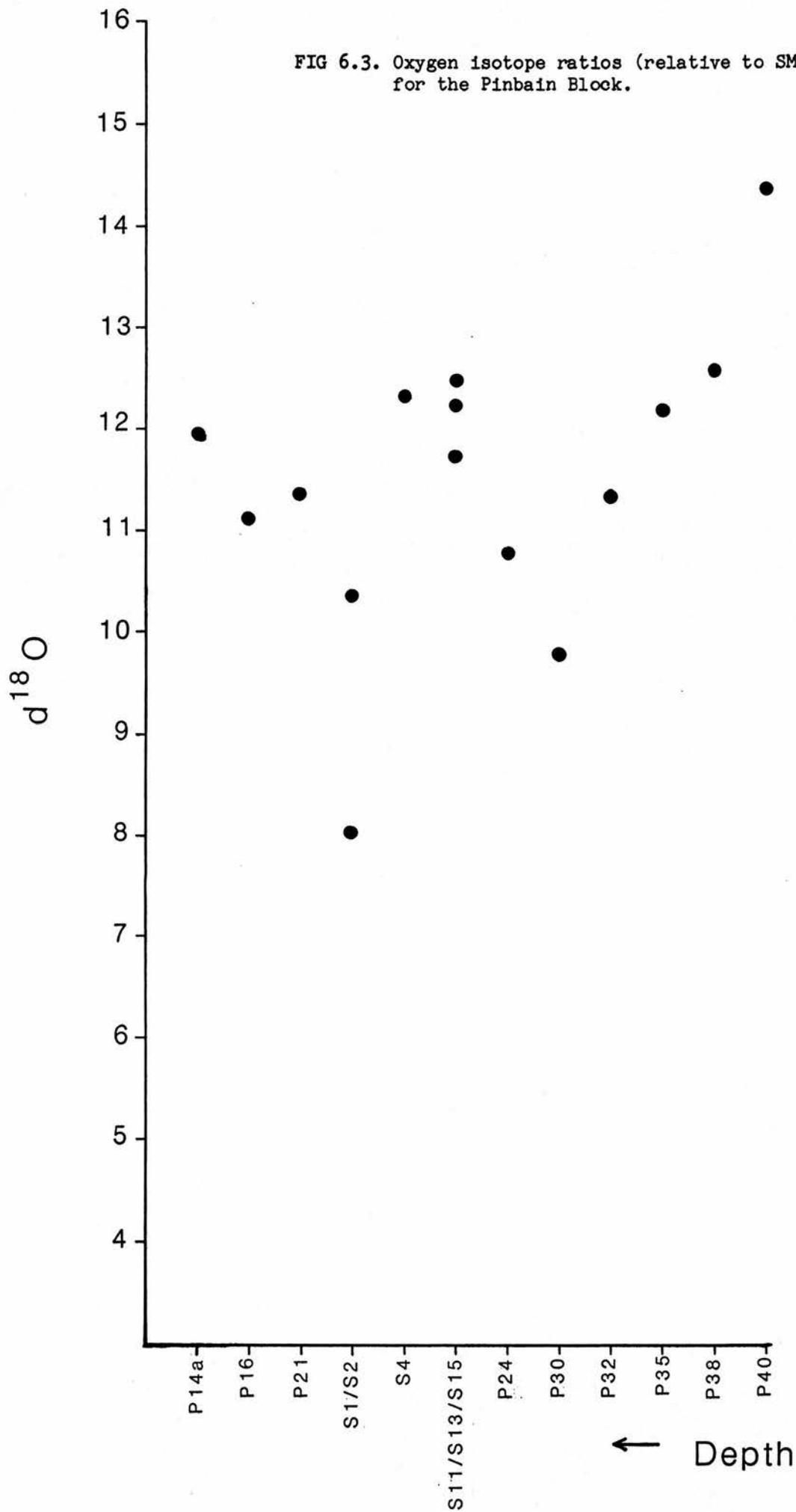
The D/H data for these rocks indicate that the fluid involved in the alteration was derived from sea water, or from the meteoric water which at the palaeolatitude of the Ballantrae Complex ( $10^{\circ}$  S) would have been very similar to sea water. It is assumed that the isotopic composition of sea water has remained constant throughout the Phanerozoic (Muehlenbachs & Clayton 1976), with  $\delta$  values of  $0 \pm 1\%$  relative to the SMOW standard.

This characterisation of the fluid allows the oxygen isotope data to be used to estimate the temperature of alteration. Fractionation curves for mineral-water systems can be calculated from the relationship:

$$\Delta_{\text{min-H}_2\text{O}} = 1000 \ln \alpha_{\text{min-H}_2\text{O}} = A (10^6/T_K^2) - B$$

The constants A and B have been calculated or experimentally determined for various minerals found in altered basalts, as shown below:-

FIG 6.3. Oxygen isotope ratios (relative to SMOW) for the Pinbain Block.



<u>MINERAL</u>	<u>A</u>	<u>B</u>	<u>Reference</u>
Chlorite	1.56	4.70	(Wenner & Taylor 1971)
Smectite	2.67	4.82	"
Quartz	3.38	2.90	(Becker & Clayton 1976)
Calcite	2.78	3.39	(O'Neil & Taylor 1967)
Albite	2.91	3.41	"

These values are used to plot curves of fractionation against temperature in fig 6.4. Because the Pinbain rocks are composed largely of metamorphic minerals (chlorite-albite-sphene), these curves define bands of possible isotope ratios which would be found in spilites which equilibrated with large quantities of water at the given temperatures. The exact delta value found depends on the modal proportions of the various minerals.

It can be seen from this graph that to produce isotope values of +12‰ the temperature must be less than 210°C, even if the rock is composed of the isotopically heaviest mineral, quartz, (which is actually rather rare in these rocks). It should also be noted that the curve for chlorite shows much lower fractionations, indicating that lower temperatures are required to produce the observed Pinbain values. Unfortunately there is no data available for sphene, a common mineral in these rocks. This means that the fractionation factors cannot be applied exactly. For the purposes of discussion it is assumed that the curve for sphene lies within the limits defined by the other curves.

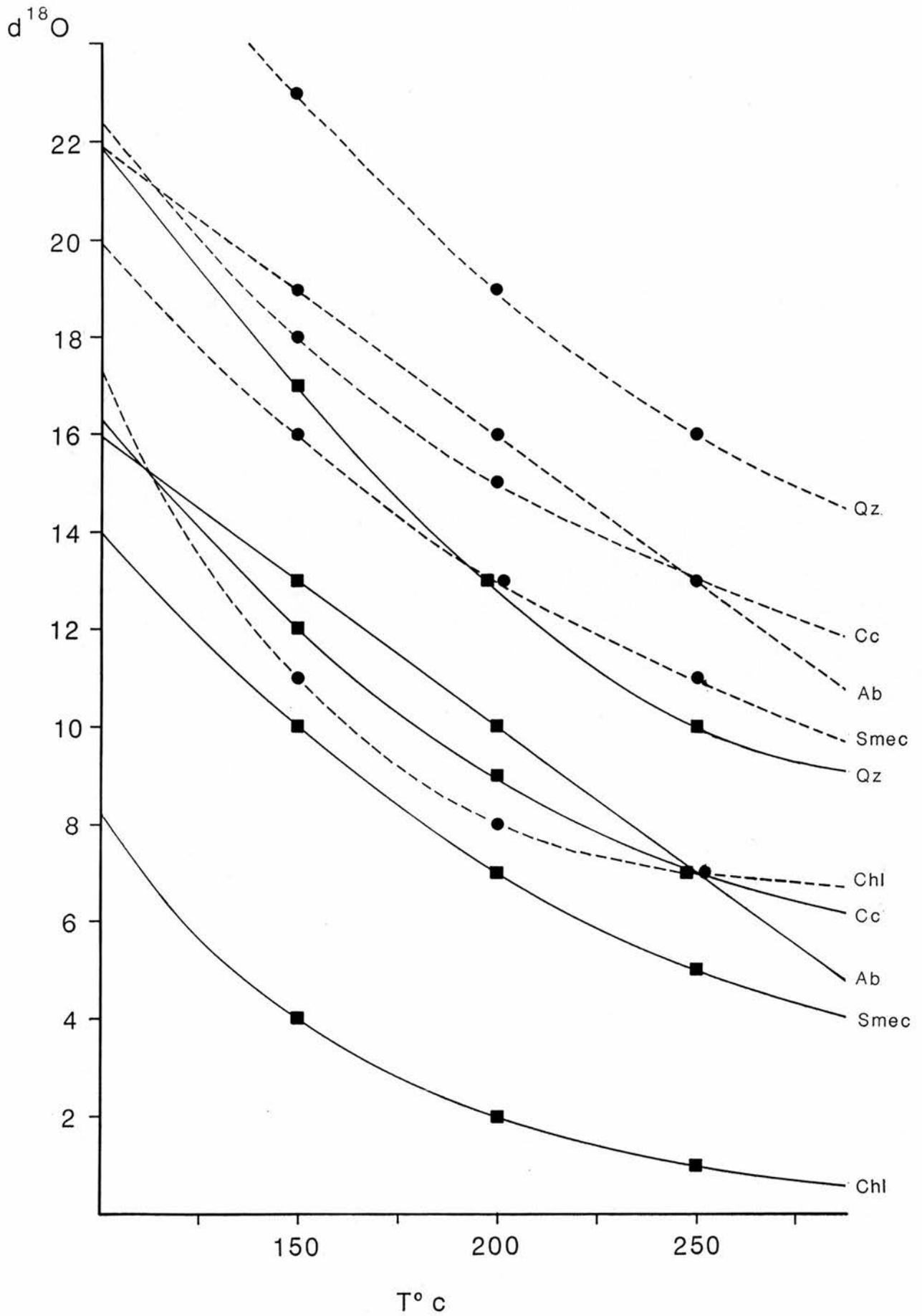


FIG 6.4. Mineral-water fractionation curves.  
 Solid lines = sea water, broken lines = magmatic water.

For a rock containing some of each of these minerals, the oxygen isotope ratios of the Pinbain rocks would be in equilibrium with sea water at a temperature of about 150-170°C.

#### 6.4.3 Water/rock Ratios

The oxygen isotope values thus indicate that the rock equilibrated with sea water at a temperature of 150-170°C. The rock values are completely reset to be in equilibrium with an unaltered water. This indicates that the water/rock ratios must have been greater than 1, so that the oxygen reservoir in the water was larger than that in the rock. In this case, as exchange occurs between the oxygen of the water and of the rock, in order to establish equilibrium, the rock's oxygen reservoir is so small that the  $^{18}\text{O}$  added to it from the water is sufficient to change the rock ratios drastically, but it is only a small fraction of the water's  $^{18}\text{O}$ , and so the oxygen isotope ratio in the water remains unchanged. If the water/rock ratio was near 1, then both ratios would change, or if the water/rock ratio was much less than 1 the water's isotope ratios would have been reset rather than the rock's. If this had happened then the final rock ratio would have been lower, and would seem to indicate higher temperatures.

#### 6.4.4 Discussion

The oxygen isotope data can be compared to the fluid inclusion temperature (250-300°C, chapter 7), and to the mineral data (analcime out=190°C, chapter 2). It is clear that the data are not compatible with equilibration with sea water at the vein temperature. The mineral temperature is in much better agreement, although still rather high.

It must be remembered that the analcime out temperature which has been experimentally determined is only a maximum, and the actual temperature represented in these rocks by the disappearance of analcime may be considerably lower, with the analcime becoming unstable by means of other reactions than the analcime-quartz reaction which has been experimentally studied. However, even if this temperature is correct there are ways in which it can be reconciled with the stable isotope data.

It is possible that the high fractionations observed in these rocks are due to lower temperature alteration of the metamorphosed rocks during the cooling process. Early sea-floor weathering would also have produced higher values, but in low temperature phyllosilicates, which are easily reset by increasing temperatures.

Another possibility is that the oxygen value of the water was higher than zero. This would happen if water from lower in the sequence had interacted with basaltic rocks at temperatures over 250°C, and with a low water/rock ratio. Under these conditions the

oxygen reservoir in the rocks would be larger than that in the water, and the isotope ratios in the water would change. Basalt has an original delta value of 5.7‰ (Wedepohl 1978), and if the fractionation factor is less than this value then the water would become enriched in  $^{18}\text{O}$ , so that the basalt and water could be in equilibrium. If this enriched fluid was then fed into the upper part of the lava pile it would mix with the sea water present and slightly increase its  $\delta^{18}\text{O}$  ratios.

In fact, fluid inclusion evidence (chapter 7) indicates that hot water was indeed moving through the relatively cool Pinbain spilites, so the possibility is open, although the hot vein systems are fairly restricted, and probably would not have cycled enough water to affect the oxygen isotope ratios significantly. The hydrogen isotope ratios would not be affected by this process because the basalts have a negligible hydrogen reservoir (they are nearly anhydrous), and the rock  $\delta\text{D}$  values would be reset rather than the waters.

Finally, the two anomalous samples, S1 and P40, need to be discussed. S1 has a  $\delta^{18}\text{O}$  value of 7.997‰. This is extremely low for these rocks. Petrographic examination shows that the rock is completely altered, so it is not a case of a relict igneous isotopic signature. This sample comes from a heavily veined area (over 50% veins in places), where fluid inclusion data indicates a fluid temperature of  $300^{\circ}\text{C}$ . The low oxygen isotope ratio can be explained by assuming that the rock was locally heated by the hot water in the veins, and therefore equilibration took place at a higher temperature, and so with lower fractionation factors, than it did in the bulk of

the Pinbain block.

At 300°C fractionation of 7.1% between rock and water is unlikely unless a lot of quartz is present, and as this is not the case this sample supports the theory that the hot water from deeper in the succession is enriched in  $^{18}\text{O}$ , suggesting that water/rock ratios were relatively low at depth.

S1 is also useful because it indicates that the fluid forming the veins was either contemporaneous with or later than the general isotopic equilibration of the rocks, otherwise the low oxygen isotope ratios would have been reset by the general alteration, and would not be consistent with the vein temperature.

P40 is a sample of basaltic conglomerate which is part of the sedimentary cover of the Ballantrae Complex. It has a rather high  $\delta^{18}\text{O}$  value which can be explained in two ways. Firstly, it is separated from the Pinbain block proper by a small fault. This fault may have sufficient throw on it to cut out a sequence with gradually declining alteration temperatures, leaving a definite break in the temperature zonation. The alternative explanation is that as a sedimentary rock, with transported and eroded clasts, the conglomerate contains a considerably higher proportion of quartz, which has a relatively high fractionation factor, thus producing an anomalously high  $\delta^{18}\text{O}$  value. It is possible for these explanations to be simultaneously true. Both explanations assume that the conglomerate and the lavas were altered by a single event. If this was not true then the lavas would have been altered before they were eroded to form

the conglomerate, and the conglomerate should then retain the original metamorphic values for the clasts. If the conglomerate was then altered to reset the clast values, the same event should be reflected in the underlying lava block, but there is no evidence there for multiple metamorphic events. The simplest explanation is that there was one metamorphic event which occurred after the deposition of the conglomerate, probably as a burial metamorphism.

The fact that there is no isotopic evidence of a high geothermal gradient (section 6.4.2) also supports the hypothesis of burial metamorphism. If the alteration was produced by heat generated or retained within the lava block then a high geothermal gradient would be expected, particularly at the top, where the lavas would be either exposed to the sea, or covered by cool sediments. A high geothermal gradient would also be expected if there was a major intrusion beneath the lava succession, which produced a locally raised temperature.

## 6.5 CONCLUSION

The stable isotope data show that the Pinbain rocks equilibrated with sea water at a temperature of approximately 150-200°C. The water/rock ratios must have been greater than 1, because the rocks have been reset to be in equilibrium with the water, rather than the water changing, or both changing to intermediate values.

CHAPTER SEVEN  
FLUID INCLUSIONS

7.1 AIMS

The purpose of this study of the fluid inclusions in veins from the Pinbain Block and the Melange is to determine the temperature and salinity of the fluids responsible for the formation of the veins. These data are obtainable by microthermometric techniques, using the assumptions detailed by Roedder (1984 chapter 9). This data will be compared with other temperature estimates to determine whether the vein formation and the alteration of the surrounding rocks were part of the same event.

7.2 EQUIPMENT

Fluid inclusion studies were undertaken at St. Andrews University, using a Linkam TH600 heating stage and controller, mounted on a Leitz microscope. Measurements were made on 50-100  $\mu\text{m}$  doubly-polished wafers, the thickness controlled by the transparency of the material. The experimental apparatus covers a temperature range of  $-180$  to  $+600^{\circ}\text{C}$ . The resolution is  $\pm 0.1^{\circ}\text{C}$  between  $-180$  and  $200^{\circ}\text{C}$ , and  $\pm 1^{\circ}\text{C}$  between  $200$  and  $600^{\circ}\text{C}$ . The accuracy of the Linkam

equipment is +/- 1.4% (Shepherd 1981).

The equipment has been calibrated using the melting points of pure standard substances (J. Kinnaird pers. comm.). Differences between standard melting points and observed temperatures were less than variations in the melting temperatures caused by impurities in the standards. The accuracy of low temperature measurements (below 0 °C) is +/- 0.05 °C, while the accuracy at high temperatures (over 100 °C) is +/- 0.5 °C (Shepherd 1981).

### 7.3 METHODS

#### 7.3.1 Sample Selection and Preparation

Samples for fluid inclusion study were chosen following the examination of thin sections. Samples containing large veins with abundant fluid inclusions were chosen, and prepared as 50-100 µm wafers, polished on both sides to ensure optimum light transmission and good thermal conduction from the heating/freezing block in the heating stage. The small size of inclusions in the samples necessitated the use of the high power objective of the microscope, giving a magnification of x430.

### 7.3.2 Freezing Measurements

Freezing experiments were carried out in order to determine the salinity of the fluid within the inclusions. The inclusions were frozen rapidly by a flow of nitrogen cooled by passage through a flask of liquid nitrogen. The inclusions were frozen down to  $-170^{\circ}\text{C}$ , then the flow of nitrogen was stabilised, and the inclusions heated up at a rate of  $10^{\circ}\text{C}$  per minute until the ice began to melt. The exact point when the ice begins to melt, the eutectic temperature of the system, could not usually be observed with any certainty even at very slow heating rates, so no attempt was made to record it, except in one inclusion in which it could be clearly seen.

When the ice began to melt the heating was halted to enable the system to equilibrate, and then continued at  $1^{\circ}\text{C}/\text{min}$ . until the ice melted, the temperature of last melting being observed. The inclusion was then refrozen, and then rapidly heated up to a few degrees below the rough last melting temperature already observed. Heating was again halted to allow equilibration, and then resumed at a slow rate,  $0.5^{\circ}\text{C}/\text{min}$ ., until the ice was nearly all melted. Heating was then halted for a few seconds, to allow a single large ice crystal to form, this being easier to observe than several small crystals. Heating was then resumed, and an accurate temperature of last melting observed.

The temperature of last melting ( $T_m$ ) of an aqueous solution is dependant on the number of dissolved ions present, i.e. the salinity. The observed melting temperature can be expressed as a salinity in equivalent weight % NaCl, according to the equation given by Potter et al. (1978). This assumes that NaCl is the only dissolved species, an approximation of natural fluids in which sodium and chloride ions predominate, although other ions also occur.

### 7.3.3 Heating Measurements

Heating of the inclusions was carried out in order to determine the temperature of homogenisation ( $T_h$ ), that is, the temperature at which the fluid becomes a single phase, rather than a liquid with a coexisting vapour bubble. This is the minimum temperature of the trapping of the fluid. As for the freezing measurements, two runs were performed, a rapid approximation first, then an accurate measurement.

The first run used a heating rate of  $10^{\circ}\text{C}/\text{min}$  until the inclusion appeared close to homogenisation, slowing to between 2 and  $5^{\circ}\text{C}/\text{min}$  for the measurement. For the accurate determination a heating rate of  $0.5^{\circ}\text{C}/\text{min}$  was used. If there was a large discrepancy ( $>2^{\circ}\text{C}$ ) between the rough and accurate measurements then the accurate run was repeated. If the accurate measurements were not in agreement then the results from that inclusion were ignored. This was only necessary on

two occasions. Discrepancies between the measurements may be caused by stretching or leakage of the inclusion, or simply by difficulty in observing the exact moment when the bubble disappears. This is often the case if the vapour bubble becomes trapped against, or in an irregularity of, the inclusion wall, when it becomes difficult to see against the dark fringe (caused by total internal reflection - Roedder 1984) of the inclusion. Careful observation during the accurate run can usually provide a reliable result, however.

#### 7.4 PETROGRAPHY OF THE FLUID INCLUSIONS

The samples selected for fluid inclusion study were from large calcite veins, rather than from the thin group 2 veins which contain a greater diversity of minerals (chapter 2). Some of the samples also contained calcite vesicles, some of which were connected to the veins. Calcite was selected because none of the other minerals in the Pinbain rocks had enough inclusions of a suitable size to be certain that the wafer would be usable.

The abundance of inclusions varied enormously between one grain and another, and also between different areas of the same grain. This may reflect the speed of crystallization, or changes in the chemistry of the fluid causing variations in the growth habit (Roedder 1981). No figures for inclusion abundance are quoted because of this extreme variability. Even where inclusions were abundant, the vast majority were too small for microthermometry, being less than 5  $\mu\text{m}$  in

diameter.

The identification of primary inclusions within these samples was extremely difficult, because there were no identifiable growth planes or zones which could be used as criteria to distinguish them from secondary or pseudo-secondary inclusions. For the purposes of this study it was assumed that all large, isolated inclusions are of primary origin. This is not entirely satisfactory, but it is supported by the fact that those inclusions occurring in trails, of obvious secondary or pseudo-secondary origin, were invariably very small, seldom exceeding 5  $\mu\text{m}$  in size, and almost never 10  $\mu\text{m}$ .

The inclusions studied ranged in size from 10 to 20  $\mu\text{m}$ . They were generally angular in appearance, of rectangular or triangular cross-section. Negative crystal shapes were not observed. All inclusions observed in the Pinbain rocks contained an aqueous fluid with a vapour bubble. The degree of fill, estimated by reference to the figures in Roedder (1972), ranged from about 5% to 20% by volume (these are very approximate estimates, because of the irregularity in the shape of inclusions).

## 7.5 RESULTS

### 7.5.1 Freezing Measurements

Relatively few freezing experiments were conducted because it was found that the melting of ice crystals was difficult to observe in the small inclusions found in these samples. Only a small proportion of the inclusions were large enough to justify the time-consuming freezing experiments. The last melting ( $T_m$ ) data are given below :-

<u>sample</u>	<u><math>T_m</math></u>	<u><math>T_h</math></u>
P36	-6.9	187
	-7.2	174
	-8.2	272
	-4.5	150
S6	-2.2	247
	-6.7	261
	-6.9	289
	-8.8	208
P20	-7.9	323

Temperatures are in degrees centigrade.

In addition to the measurement of the temperature of last melting, in one inclusion in the sample S6 it was possible to measure a temperature of first melting, which was  $-28.3^{\circ}\text{C}$ .

#### 7.5.2 Heating Measurements

42 homogenisation temperatures were determined from the Pinbain samples, including 1 from an inclusion which may be secondary, because it occurs in close proximity to a train of secondary inclusions. These data are given in the table below, with the doubtful inclusion marked with an asterisk, and inclusions from vesicles rather than veins marked with a v.

P20 :-	323	318	341
Prehnite zone	307	324	249-v
S6 :-	157	247	148
Transition zone	189	299	235
	229	217	261
	289	208	249
	238	202-v	255-v
	265-v	255-v	

P28 :-	100	252	171
Analcime zone	164	156	180
(base)	228	210	214
	152	137	138
P36 :-	187	174	272
Analcime zone	296	131	186
(top)	150*		

These temperatures are in degrees centigrade.

These data are also plotted in the histograms, fig 7.1, which will be discussed below.

## 7.6 EXPLANATION OF FREEZING DATA

### 7.6.1 Eutectic Temperature

The measurement of a eutectic (first melt) temperature of  $-28.3^{\circ}\text{C}$  allows some determination of the composition of the fluid to be made. The eutectic point of an NaCl-water system with a salinity of less than 23.3% is  $-20.8^{\circ}\text{C}$  (Roedder 1962). The observed temperature is closer to this than to eutectic temperatures for other pure solutions

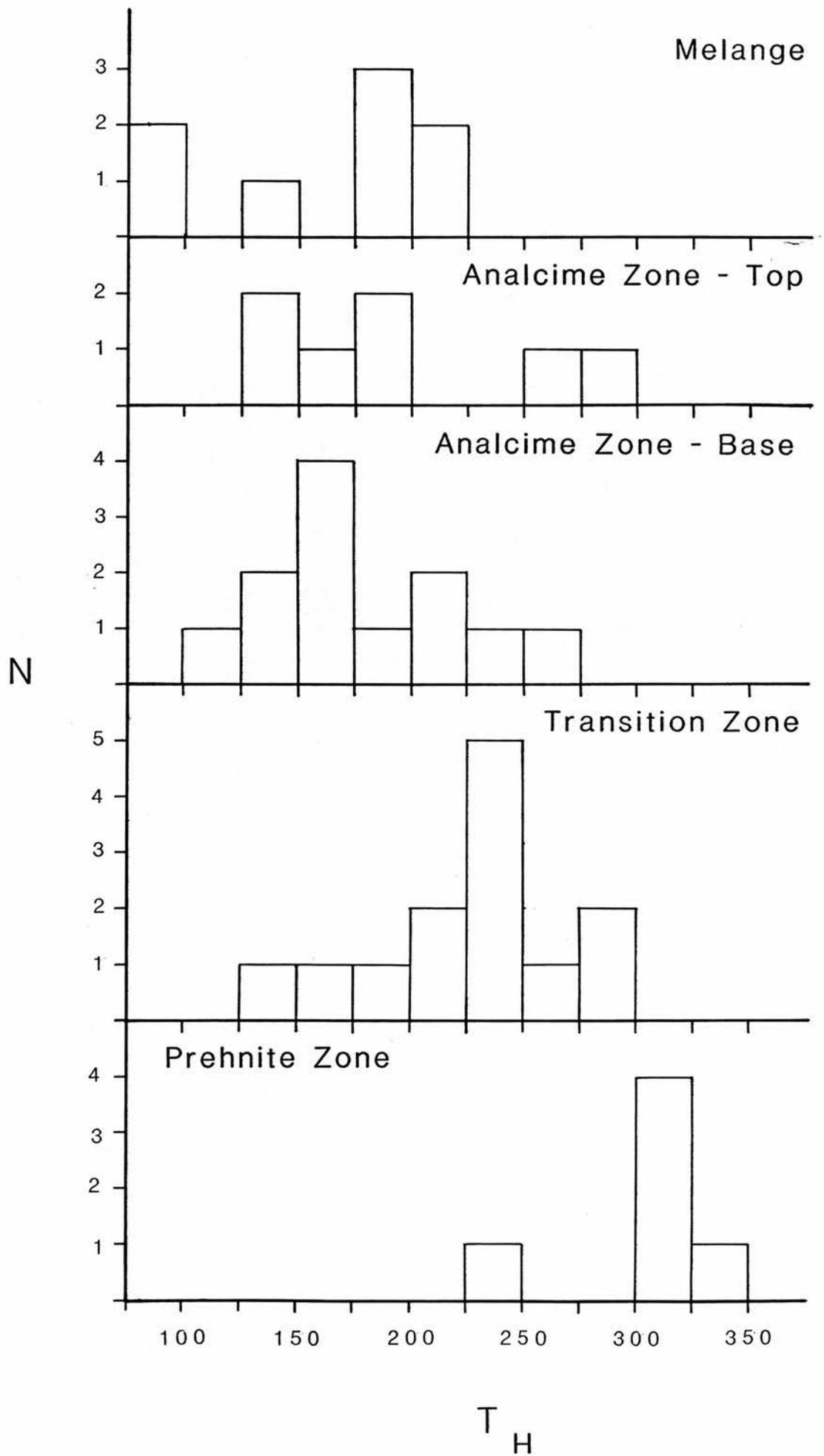


FIG 7.1. Histograms of homogenisation temperatures of the fluid inclusions of the Pinbain Lava Block and melange.

of geological interest, eg  $\text{CaCl}_2$ ,  $-50^\circ\text{C}$ , while the eutectic point for aqueous  $\text{KCl}$  is  $-10^\circ\text{C}$ . The fact that the first melting temperature is not equal to the eutectic temperature indicates that although  $\text{NaCl}$  is probably the main constituent there must be other ions present, calcium almost certainly being important, judging by the amount of calcite being deposited by these solutions!

### 7.6.2 Salinity

The measurement of the depression of freezing point enables the salinity to be calculated according to the equation derived by Potter et al. (1978) :-

$$W \pm 0.028 = 0.00 + 1.76958 F - 4.2384 \times 10^{-2} F^2 + 5.2778 \times 10^{-4} F^3$$

where  $W$  is the weight percent  $\text{NaCl}$  equivalent, and  $F$  is the freezing point depression in degrees centigrade.

The salinities calculated for the Pinbain rocks are given in the table below :-

<u>Sample</u>	<u>Tm</u>	<u>salinity</u>
P20	-7.9	11.6
S6	-2.2	3.7
	-6.7	10.3
	-6.9	10.4
	-8.8	12.6
P36	-6.9	10.4
	-7.2	10.7
	-8.2	11.9
	-4.5	7.1

Temperatures are in degrees centigrade, and salinities in weight % NaCl equivalent.

These data are fairly consistent, generally indicating a salinity between 10.3 and 12.6%. There are two anomalous results, 3.7% and 7.1%. Of these the figure of 3.1% may be due to an experimental error because it plots well away from the other results on the graph of temperature versus salinity (fig 7.2). The other result however, 7.1%, is probably genuine because it plots in the same trend as the other results. This trend will be discussed in the next section.

It is clear from the salinities given above that the vein fluid is much more saline than the sea water which was the major fluid involved in the alteration of the Pinbain rocks (chapter 6). Normal sea water has a salinity of approximately 3% (Roedder 1984) at the present day, and is not believed to have been significantly different in the past. The concentration of the Pinbain fluids was not the

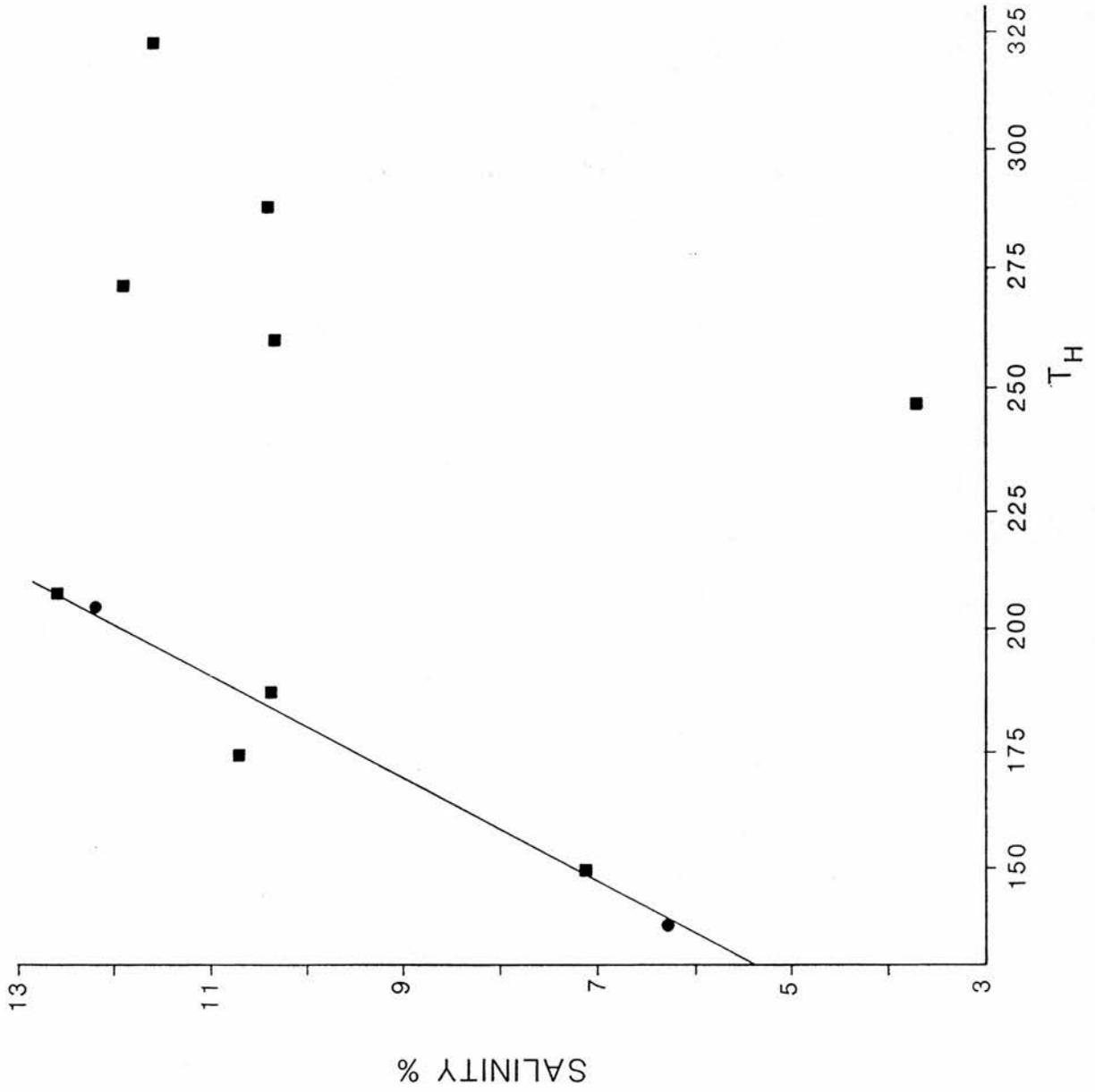


FIG 7.2. Temperature-salinity relationships for the Pinbain fluid.

result of evaporation, because the evaporation process would have changed the stable isotope ratios. The extra dissolved material is probably derived from rocks which the water passed through as it penetrated the crust. The high salinity however makes it unlikely that the alteration fluid was derived from meteoric water, which would start with a very low salinity.

The salinity recorded in these rocks is well within the range of 2 to 16% NaCl equivalent reported by Jehl (1975) for hydrothermally metamorphosed basalts dredged from the North Atlantic ocean floor. These rocks ranged from the zeolite to the prehnite-pumpellyite facies, with homogenisation temperatures of between 124 and 335°C.

#### 7.7 FLUID TYPES

The graph of salinity against homogenisation temperature (fig 7.2) can be used to distinguish two trends, representing two different fluids. The trends are clearest when the data for the Pinbain melange are included (these are included in the graph but are discussed separately in section 7.9 below). There is a relatively low temperature fluid (<215°C), for which there is a positive correlation between salinity and homogenisation temperature, i.e. the higher the temperature the more dissolved material is carried. The second fluid is relatively high temperature (>245°C), with a high salinity of between 10 and 12% NaCl equivalent. There is also an anomalous result with a temperature of 247°C associated with a salinity of 3.7%. This result may well be a result of an error in measurement, as discussed

above. If it is a genuine result it would appear to represent a third fluid of unknown provenance.

A study of the homogenisation temperatures supports this two-fluid theory. From the histograms (fig 7.1) it can be seen that a temperature of approximately 200°C divides the low temperature from the high temperature inclusions. This is clearest in the histogram for P36 which is distinctly bipolar. P28 is slightly bipolar, but is dominated by low temperature inclusions, in contrast to the predominantly high temperature inclusions in S6. In P20, from the prehnite zone, all measured inclusions came from the high-temperature population.

#### 7.8 DISCUSSION

There are two theories which can explain these data. Since the two fluids occur in the same veins it is possible that the lower temperature-salinity fluid occurs in secondary inclusions which were not identified as such, and the fluid contained in them is that which was present in the rocks as they cooled down after the peak of the metamorphism. Alternatively, there could have been two fluids co-existing within the rock at the time of veining.

This second theory is supported by the fact that the stable isotope evidence (chapter 6), the analcime-out isograd (chapter 2), and the chlorite temperatures (chapter 4) show that the bulk of the rock was at a much lower temperature than the high temperature inclusions within the veins. In this interpretation the low temperature fluid represents the water filling the pore spaces in most of the lava succession. This explains its relative coolness, it being at approximately the temperature of the rocks, as indicated by mineral and stable isotope data. This fluid has a salinity which is dependant on its temperature, presumably deriving its dissolved material from the rocks it passes through, and dissolving more as its temperature increases.

The second fluid is relatively high temperature, and it has a relatively high salinity which is independant of the temperature of trapping. This fluid is probably derived from deeper in the succession, where it was heated to about 350°C, the temperature recorded from veins in the prehnite zone.

Since both fluids are detected in inclusions of (probably) primary origin from the same vein, and in some cases from the same crystal, it is clear that there was not a steady flow of a single fluid in the fracture system. It is possible that individual veins may not have been active continuously, and that changes in the flow pattern of the hot fluid allowed cooler water to enter the vein system. In the samples P28 and S6 there are intermediate homogenisation temperatures that could reflect this mixing. There are

several possible mechanisms for changing flow patterns, e.g. veins could become 'plugged' by growing crystals, or minor faulting or shifting of clasts within the sediments could change the flow system.

When the flow pattern changes, then the fracture systems fill with the cool pore fluid, but crystallization of the calcite is not interrupted, thus allowing the low temperature inclusions to form in the same crystals as the high temperature inclusions. Calcite is stable over a wide range of temperatures (Winkler 1979), and provided that the fluids are chemically able to deposit calcite there is no problem inherent in this continuous crystallization.

High temperature inclusions are not restricted to a single, definite zone within each crystal, so it appears that there were several, perhaps many pulses of high temperature fluid during the lifetime of the vein systems.

The lack of low temperature inclusions in the sample from the prehnite zone, P20, may indicate that the vein system was sealed off from the pore fluids in this area, and that only the hot water moved through the veins. The ascending hot water spread out and the vein system became more open higher in the succession, so the high temperature fluid cooled rapidly (fig 7.2). The prehnite zone contains for the most part relatively massive and unbrecciated lavas, and so has a lower porosity/permeability than the rest of the section, and this may explain why the veins in this area remained closed to the cooler fluid - it was unable to permeate in with any speed.

## 7.9 PRESSURE CORRECTION

The temperatures quoted in the results and discussions above are all uncorrected homogenisation temperatures. To be more accurate it is necessary to correct the temperature to take into account the effects of pressure (Roedder 1984). This is the somewhat misleadingly named 'pressure correction'. The lithostatic pressure at the top of the Pinbain section is that due to the weight of the overburden, which consists of approximately 4 km of sediment (chapter 8). This would produce a lithostatic pressure of about 1 kilobars, using a normal geobarometric gradient of 0.3 kb/km.

Potter (1977) has produced graphs of pressure correction against homogenisation temperature for fluid inclusions of various salinities at different pressures. The salinities of the Pinbain inclusions are generally between 10 and 12.5% NaCl equivalent, so the graph for 10% salinity was used. Roedder (1982) has demonstrated that assuming a salinity of 10% will not introduce major errors for the few inclusions with different salinities.

Using Potter's graphs it can be seen that a pressure correction of 60°C must be applied to the homogenisation temperatures, assuming that the vein systems were under lithostatic pressure. This assumption will now be examined.

In the first place it is unlikely that the assumption of lithostatic pressure is justified within the Pinbain section. The large number of open pore spaces, vesicles, veins and gaps between irregularly shaped blocks in the breccias suggests that the rocks were rigid enough to support their own weight and the overburden without the pore spaces collapsing. This means that there is no way for the lithostatic pressure of the rock framework to be transmitted to the fluid in the pore spaces. If this is the case then the pressure difference between the top and the bottom of the Pinbain succession would be due solely to the weight of the water column, an amount which is not important in geological terms. This means that the same pressure correction can justifiably be applied to the bottom of the section as to the top.

This reasoning cannot be applied to the sedimentary cover of the Pinbain Block, however. The sediments range from the coarse conglomerates of the Kilranny and Benan conglomerate to the fine sands and shales of the Ardwell Group and succeeding members (Williams 1962). These sediments are much less rigid than the rocks of the Pinbain Block, without the open, rigidly supported pore spaces, and it is likely that pore fluids within them would be under lithostatic pressure. Since the stable isotope data (Chapter 6) suggest that there was a circulation of water derived from these sediments within the Pinbain Block, it seems clear that the pressure within the Block would be equal to that at the top, controlled by the lithostatic pressure within the overlying sediments. The water circulation from beneath the lava block is probably controlled by density differences,

and will not affect the pressure considerations.

Finally, it should be noted that this discussion of the pressure correction does not affect the reasoning used to produce the model detailed above - it only changes the details of temperature.

#### 7.10 THE PINBAIN MELANGE

One sample from the Pinbain melange (P7) was examined. The details of the experiments was the same as for the samples from the Pinbain Block proper. Three inclusions which were examined proved to be secondary, but eight primary inclusions were examined, two of which provided freezing measurements as well as homogenisation temperatures. The results are given below :-

<u>Primary</u>			<u>Secondary</u>
Th	Tm	Sal	Th
138.8	-4.1	6.6	116.8
205	-8.4	12.2	118.4
201			130.1
198.7			
93.5			
178.5			
76.4			
196.3			

Temperatures are in degrees centigrade. Sal = salinity in weight % NaCl equivalent.

The sample P7 is one of the fine grained sediments from the melange. It was chosen because the veins in it must postdate the assembly of the melange, unlike some of the coarser-grained sediments in which the clasts contain veins which predate the formation of the melange, and which would therefore not provide information about the subsequent metamorphism of the Ballantrae Complex.

As was noted above (section 7.6.3) the inclusions from the Pinbain melange provide data which fit the salinity-temperature trend for the low temperature fluid from the Pinbain Block proper (fig 7.2). These data indicate that the melange was probably adjacent to the Pinbain Lava Block at the time of vein formation, and that it formed part of the same hydrothermal system. However, judging from the lower temperatures recorded (fig 7.1) it is probable that it was at a higher level in the crust at the time of veining than its present position faulted in at the base of the lava block. The homogenisation temperature histogram (fig 7.1) appears to show a bipolar distribution, but the salinity diagram shows that the 200°C temperature is for the cool fluid, and the lower temperatures recorded probably show a cooling sequence.

The secondary inclusions recorded seem to be the same temperature as the primary inclusions. These might represent the cooling sequence as well, in which case they would form at the same time as the cooler primary inclusions, but in older parts of the crystal, which had originally grown at a higher temperature.

## 7.11 CONCLUSIONS

Fluid inclusions in group 1 veins in the Pinbain lava block and the Pinbain melange show that calcite crystallized in these veins at temperatures of 300°C or more. There are also inclusions formed at lower temperatures which correspond much more closely with temperatures estimated for the Pinbain succession by other methods. Temperature-salinity trends suggest that these two types of inclusion represent two different fluids, which coexisted in the succession. The bulk of the section was probably occupied by the relatively low temperature fluid, which shared the same temperature as the rock. The hot fluid was restricted to the veins.

CHAPTER EIGHT

DISCUSSION

8.1 METAMORPHIC CONDITIONS

8.1.1 Temperature

Several different techniques have been used to estimate the temperature of the Pinbain Block during metamorphism. The only useful change in mineralogy in the section is the disappearance of analcime below the transition zone. This gives a maximum temperature of 190°C (chapter 2). The chlorite geothermometer (chapter 4), indicates temperatures between about 150 and 250°C. Oxygen isotope studies indicate that the rocks were in equilibrium with sea water at a temperature of 150-170°C (chapter 6). All these techniques are in broad agreement, and it is safe to conclude that the base of the Pinbain Block reached a temperature of about 200°C, while the top of the succession was somewhat cooler, between 150 and 200°C. The techniques are not sufficiently precise to enable the geothermal gradient to be estimated, but this in itself indicates that it could not have been much higher than normal, because a difference of >50°C between the base and the top of the succession would probably have produced noticeable differences in the isotope ratios and the chlorite temperatures.

The fluid inclusions indicate maximum fluid temperatures of 250-350°C (chapter 7), with a steep temperature gradient (in contrast to the isotope data). There are also lower temperatures recorded which are close to the those estimated using other methods. It is probable that the higher temperatures recorded represent the temperature of the fluid flowing through the major veins. The veins were thus conduits for hot fluid presumably derived from deeper in the crust.

#### 8.1.2 Metamorphic Fluids

Fluid inclusion and stable isotope data have enabled an evaluation to be made of the nature and temperature of the fluid present during metamorphism.

The hydrogen isotope ratios (chapter 6) show that the main body of the spilites was altered by either sea water, or meteoric water. These two waters cannot be isotopically distinguished in the low palaeolatitudes which the south of Scotland occupied during the Ordovician and Silurian. However, since the Pinbain lavas are a marine succession with the possible exception of a few flows with reddened tops (Smellie 1984a), and the Ordovician and Silurian sedimentary sequences above the complex are exclusively marine (Anderton et al. 1979), the water was almost certainly sea water.

The sea water is responsible for the alteration of the bulk rocks and the resetting of the isotope ratios. The integrated water/rock ratios for this fluid must have been  $>1$ , to allow complete equilibration of the rock isotope ratios to the unmodified water. This shows that the water must have been moving through the succession, because this amount of water could not all be held within the rocks at one time. It probably moved slowly downwards into and through the succession by percolating through cracks and fissures, and it also filled voids in the rocks, such as the vesicles containing analcime, which grew at a temperature of  $<190^{\circ}\text{C}$ . The oxygen isotope ratios of the rocks indicate that the temperature was  $150-170^{\circ}\text{C}$ .

In addition to this fluid there was also a relatively high temperature fluid, which moved forcefully upwards through the Pinbain Block fracturing the rocks, or utilising pre-existing fractures, to form relatively localised veins. This fluid cooled rapidly as it moved upwards through the cooler Pinbain Block, and probably began to mix with cool sea water towards the top of the presently exposed Pinbain section, producing veins with lower temperature fluid inclusions at the top of the analcime zone.

The combination of a relatively cool fluid passing through the Pinbain Block with a hot fluid moving upwards through veins suggests that there was an active hydrothermal circulation taking place. Sea water would percolate downwards through the sedimentary sequence and the Pinbain Block to a deeper level in the crust, where it would be heated up, to return towards the surface in relatively localised vein

systems. Movement of sea water in the downward leg of the cycle may have been facilitated by the presence of faults which Williams (1962) has suggested were active during sedimentation.

## 8.2 CAUSE OF METAMORPHISM

Petrographic evidence (chapter 2) shows that there was a single metamorphic event, associated with one generation of veining. There is no indication of any alteration having taken place before the analcime-prehnite zoning now observed was established, although there may well have been some hydration of the volcanic glass matrix, and the formation of clays and/or chlorite as the sequence was buried. There is a certain amount of retrogressive smectite development at a late stage, but the picture is one of a single main phase of alteration/metamorphism. The question is, when did this take place, and what was the cause?

The metamorphism obviously post-dates the eruption of the lavas in the Arenig. It was not an autometamorphism of hot lavas, because the sequence contains too much sediment for retained heat in the pile to have been significant, and in any case, the lavas are so brecciated and permeable that they must have cooled very rapidly after they were erupted into shallow water. The metamorphism must predate the Caledonian deformation of the Ballantrae Complex into its present steeply dipping attitude, because the metamorphic zones are more or less parallel to the bedding, and have been deformed with it. This deformation took place during lower and middle Old Red Sandstone

times, in the Devonian (Walton 1983).

The Kilranny Conglomerate shares the metamorphism, of the Pinbain Block, and in addition, graptolites from the Ardmillan Group at Laggan Gill, to the north-east of, and stratigraphically above the Pinbain Block, have graptolite reflectance values of 0.6 (G. Oliver pers. comm.). This is equivalent to a temperature of  $125^{\circ}\text{C}$ , using the correlation given by Price (1983) for vitrinite reflectance. This is close to the temperature of about  $150^{\circ}\text{C}$  at the top of the Pinbain Block, which suggests that the temperatures were developed in the same event. Since the metamorphism occurred prior to deformation, and affected the sedimentary cover as well as the Pinbain Block, it can be considered to be a burial metamorphism.

The estimated thickness of the Ordovician sedimentary pile above the Ballantrae Complex is up to 3160 m at the northern end (Whittington 1972), although there are considerable thickness variations, and the actual thickness in any one place is more likely to be about 2500 m. This is overlain with slight unconformity by another 1000 m of Silurian marine sediments (Walton 1983). Studies of burial metamorphism elsewhere in the world have given depths of 3000 m for zeolite facies metamorphism of basalts in New Zealand (Leitch 1978) and the same depth for the prehnite-pumpellyite facies in Puerto Rico (Jolly 1970). Hawkins (1967) has suggested a depth of 3000 m for prehnite occurrences in shales and greywackes on Mt. Olympus, Washington. Since the Pinbain Lava Block has been buried beneath some 3500 m of sediments it is quite comparable to other areas which have undergone burial metamorphism.

The Silurian sedimentary succession at Girvan passes up conformably into lower Old Red Sandstone continental sediments, and metamorphism may have continued into Old Red Sandstone times, utilising pore water within the Pinbain Block. The main period of metamorphism, however, required large quantities of unaltered water, which would not have been available during Old Red Sandstone times, because the semi-arid climate (Anderton et al. 1979) would not allow the penetration of large quantities of water into the succession.

The temperature of the transition zone of the Pinbain Block is at most  $190^{\circ}\text{C}$ . This is about 1 km below the top of the Pinbain Block, and has thus suffered burial to a depth of 4.5 km. This implies that there was a geothermal gradient of about  $40^{\circ}\text{C}/\text{km}$ , assuming that the maximum temperature was developed at the time of maximum burial. This gradient is slightly higher than the normal geothermal gradient for continental areas, but it was established at the end of the Silurian or the beginning of the Devonian, when Caledonian orogenic activity was taking place, and in particular, at much the same time as the intrusion of granites in the Southern Uplands. This orogenic activity could well have been responsible for higher geothermal gradients in the neighbouring Midland Valley. The two terranes were probably in their present positions by this time, since Silurian sediments in the Midland Valley are derived from a greywacke terrane to the south (Walton 1983).

Another possible explanation for the high geothermal gradient is the fact that hydration reactions in basalts are exothermic. Fyfe (1974) has shown that the heat produced by these reactions is not negligible, and it could have been responsible for raising the temperature of the Pinbain Block, and other parts of the Ballantrae Complex above that which would be expected for the depth. However, the amount of water which circulated through the Pinbain Block was probably enough to carry away the heat produced in this manner, and so prevent any significant increase in temperature.

There is no evidence that analcime, one of the zone minerals, was ever present in the prehnite zone. This suggests that the growth of analcime only began after the thermal conditions represented by the zoning had been established. If it had grown earlier then the prehnite zone should contain relict analcime, perhaps as an early lining of amygdales, or albite formed by the decomposition of analcime. The growth of analcime is probably related to the circulation of sea water through the Pinbain Block, since analcime is sodium rich, and it is largely restricted to vesicle occurrences. If this circulation of sea water only began when the succession reached its maximum temperature, this would explain why the formation of analcime was restricted to the analcime zone. Most of the metamorphism appears to have occurred simultaneously, and it is likely that the circulation of water was as important a factor as the temperature, because it ensured that there was plentiful fluid to allow hydration reactions, and to transport elements to growing crystals.

There may have been some metamorphism before the peak temperature was reached, and this may account for the spread in temperatures estimated using the chlorite geothermometer (chapter 4). The metamorphism probably ended quite abruptly when Caledonian deformation, followed by uplift and erosion, took place, with only a slight development of retrogressive smectite during the cooling period.

#### 8.2.1 Hydrothermal Activity

The Pinbain lavas have been altered with sea water/rock ratios of between 1 and 10. This, and the fact that veins passing through the Pinbain Block contained a fluid which was hotter than the main body of the succession, and the sea water which it contained, indicates that there was an active hydrothermal circulation taking place. The water passing up through the section from deeper in the crust must have been heated somehow. There are several possible heat sources. The first possibility is that there is an intrusion somewhere beneath the Ballantrae Complex, which has not been discovered. A second possibility is that the hot fluid had been heated at a deeper level in the crust, which was hotter because of the normal geothermal gradient. Gillis & Robinson (1988) have suggested a mechanism by which temperature contrasts can develop in ophiolite successions. The upper layer of the crust is porous, and contains large quantities of cold sea water. The Pinbain Block is equivalent to this layer. Because of the large quantities of water, heat flow is rapid, and the

upper layer cools rapidly. The lower part of the ophiolite is relatively impermeable, however, and can transfer heat only by conduction, and so its temperature rises relative to the upper layer. A temperature gradient develops at the boundary between the two layers, and heat transfer at this boundary layer can start convection cells in the fluid bathing the upper layer. Since the Pinbain Block has had large quantities of sea water passing through it, if there was a relatively impermeable layer beneath the succession it is possible that this mechanism could occur, even if the only heat source was the normal crustal heat flow.

Since it was suggested in the previous section that the hydrothermal circulation only began when temperatures approached their maximum, it may be that the circulation was started by an intrusion, or possibly by an increased crustal heat flow associated with Caledonian magmatic activity

### 8.3 THE PINBAIN MELANGE

The Pinbain melange differs from the Pinbain Lava Block in several ways. In the first place the lithology is different, with the lavas and lava breccias in the melange having probably been transported a considerable distance, whereas the lavas in the Pinbain Block are in situ, and the breccias and conglomerates are derived from within the succession. To emphasise this fact, the melange contains clasts of metamorphic rocks which show that there has been an episode of metamorphism prior to the formation of the melange. The lava

breccias in the melange also show evidence of a previous metamorphism, in that some of the veining occurred prior to the formation of the clasts, whereas some cuts both clasts and matrix, and clearly post-dates the formation of the melange. This supports the work of Bluck (1985) who suggested that the olistostrome units within the Ballantrae Complex may contain material from an older ophiolite, which is no longer exposed.

Prehnite occurs in late veins in the melange, which would suggest that the conditions in the melange were similar to those in the prehnite zone of the Pinbain Block. However, the veins it occurs in are group 1 veins, which are formed by hot water moving upwards, and so the prehnite provides no evidence for the temperature of the rock. Graptolite fragments from the black shale matrix of the melange have reflectance values of 1.8 (G. Oliver pers. comm.), which indicate temperatures of  $275^{\circ}\text{C}$  (Price 1983). This temperature is high enough for the formation of the prehnite and pumpellyite which have been found in lava clasts in the melange (Smellie 1984b), and suggests that the prehnite-pumpellyite facies assemblage developed after the assembly of the melange, and not during the alteration event represented by the early generation of veining.

Since the Pinbain Melange was metamorphosed under prehnite-pumpellyite facies conditions, it is likely that it occupied a position similar to its present one, i.e. below the base of the Pinbain Block (when the effects of Caledonian deformation are removed). This creates a problem with the fluid inclusion data (chapter 8), which shows that the vein fluid in the melange was

similar to that in the Pinbain Block, but was actually cooler than the graptolite reflectance temperature. If the melange was deeper in the crust than the Pinbain lavas, the low temperature/salinity fluid, which is the pore fluid of the rock, would be expected to be hotter than it is.

This problem is difficult to resolve. It suggests that the Pinbain Melange underwent a more complex history than the lava block, and that the veins were not contemporaneous with the prehnite-pumpellyite facies metamorphism. There are three possible explanations:-

1). The temperature-salinity relationships of the fluid inclusions suggest that the fluid in the veins of the Pinbain Block and the melange were the same. If this is true, then the melange would have to be higher in the crust, than the Pinbain Lava Block, because the melange veins are cooler. The prehnite-pumpellyite facies metamorphism of the melange must have been earlier than the burial metamorphism of the lava block, which was contemporaneous with the veining.

2). The prehnite-pumpellyite facies metamorphism of the melange was part of the same burial metamorphic event as that of the Pinbain Lava Block. The cool veining could not have formed at this time, because the rock temperature was higher than the vein temperatures. The veins could have contained the same fluid that filled the veins in the lava block, but at either a relatively early stage, before the peak temperature had been reached, or a relatively late stage, when

the succession was cooling. The absence of hotter veins could indicate that flow patterns of the hydrothermal system changed as the area was heating, or as it started cooling.

3). The metamorphism of the Pinbain Lava Block and the melange was simultaneous, but the resemblance between the vein fluids is purely accidental. The veins in the melange could be either early or late in the metamorphic history, forming either during the heating up of the area, or during its cooling.

Of these explanations, 2 and 3 are to be preferred, because they do not require the assumption that an episode of metamorphism occurred between the formation of the melange and the burial metamorphism of the Pinbain Block.

#### 8.4 SYNTHESIS

Both the Pinbain Lava Block and the Pinbain Melange show evidence for a burial metamorphism up to the prehnite-pumpellyite facies. This occurred before the Pinbain section was deformed into its present near vertical attitude, but the relative positions of the lava sequence and the melange could have been as they are now, i.e. with the melange structurally below the lava sequence.

The juxtaposition of lavas and serpentinites of different provenances block-faulted together, as in the Ballantrae Complex, is quite characteristic of fore-arc regions, and it seems likely that the burial metamorphism followed the filling of an Ordovician fore-arc basin (Bluck 1983), which developed into an upper slope basin in the Silurian (Walton 1983).

There is no evidence that the Pinbain lavas underwent a complex history before undergoing the burial metamorphism. In contrast to the Pinbain Melange there is no evidence for a previous metamorphic episode, and the only previous structural event was a slight tilting, which resulted in the Ordovician sediments being deposited on the Pinbain Block with  $<30^{\circ}$  of unconformity (Williams 1962). This deformation may have been associated with the assembly of the Ballantrae Complex some time between the Arenig and the Llandeilo. The lack of a complex history suggests that the Pinbain lavas, which are of intraplate origin (chapter 5), are more or less in situ. There is additional evidence for this in that dykes of similar intraplate chemistry, which also contain titaniferous augite, have been reported by Holub et al. (1984) to cut the dynamothermal aureole of the northern serpentinite, and thus to postdate the obduction of the mantle rocks represented by the serpentinite. The dykes show some LIL enrichment, which may have resulted from the magma having been generated in a mantle wedge above a subducted slab, suggesting that it was intruded in a fore-arc region. Since they have a similar chemistry, the Pinbain lavas may well be part of the same magmatic episode.

The geological history of the Pinbain Lava Block can be summarized as follows:-

1). The Pinbain lavas are erupted in a fore-arc area, which consists of largely ophiolitic rocks, including the other elements of the Ballantrae Complex.

2). The Pinbain lavas are slightly deformed as the Ballantrae Complex is tectonically assembled.

3). The area is covered by c. 2500 m of Ordovician deep sea sediments, derived from a continental arc to the north.

4). After a hiatus, and slight deformation, Silurian sedimentation deposits 1000 m of sediments, probably derived from the Southern Uplands to the south (Walton 1983).

5). Towards the end of the Silurian a burial metamorphism occurs, assisted by the circulation of large quantities of sea water, and possibly by increased heat flow related to Caledonian orogenesis. The Pinbain Block is metamorphosed to the zeolite and prehnite-pumpellyite facies, with a temperature of about 150<sup>o</sup>-200<sup>o</sup>C. The melange is also metamorphosed to the prehnite-pumpellyite facies, at a higher temperature.

6). In lower and middle Old Red Sandstone times the area is deformed, uplifted and eroded. The Pinbain Block is deformed into its present attitude and metamorphism ceases, after some retrogression of chlorite to smectite. The veining in the melange may have occurred at this time.

#### 8.5 SUGGESTIONS FOR FUTURE RESEARCH

The metamorphic history of the rest of the Ballantrae Complex is known only in general terms (e.g. Smellie 1984). Detailed work on the other lava blocks of the complex, along the same lines as this project, is needed. For the Pinbain Block itself, more information is needed on the relationship between the veins of groups 1 and 2. This would require more fluid inclusion work, and also stable isotope studies of mineral separates. Stable isotope studies of mineral separates from the bulk rock could be used to provide a more exact indication of the temperature of metamorphism. The sedimentary cover of the Ballantrae Complex should also be studied, to define the conditions existing during burial.

### CONCLUSIONS

1. The Pinbain lava sequence is composed of intraplate tholeiitic basalts.

2. After slight deformation, probably associated with the assembly of the Ballantrae Complex, the Pinbain Block was buried under 3-4 km of Ordovician and Silurian sediments. There is no evidence for alteration having occurred prior to this event. In particular, spilitisation did not occur while the lavas were still hot on the sea floor, as suggested by Bluck (1981).

3. The Pinbain Melange does show signs of an alteration event affecting lava clasts, which must have occurred prior to the assembly of the complex.

4. The Pinbain Lava Block was metamorphosed to the prehnite-pumpellyite facies in the prehnite zone at the base of the succession, and to the zeolite facies in the analcime zone at the top. The Pinbain Melange was metamorphosed to the prehnite-pumpellyite facies, probably in the same event. The metamorphic zonation is approximately parallel to the strike of the lava succession.

5. The metamorphism was a burial metamorphism, and affected the sediments overlying the lava block, as well as the lavas. Experimental evidence suggests that the boundary between the analcime zone and the prehnite zone represents a temperature of  $<190^{\circ}\text{C}$ . Stable

isotope evidence indicates that the temperature of most of the Pinbain Block was 150-170°C. Sediments stratigraphically above the Pinbain block have a graptolite reflectance temperature of approximately 125°C.

6. The alteration of the Pinbain Block took place in the presence of large quantities of sea water. Stable isotope evidence shows that the isotope system was water-dominated, and the water/rock ratio was between 1 and 10. The large quantities of water passing through the rock caused mobilisation of many elements, resulting in changes in the bulk chemistry.

7. The Pinbain Block is traversed by large calcite veins, which have fluid inclusions indicating a temperature of 300-350°C. These veins are derived from a hot source somewhere below the Pinbain Block. The Pinbain Melange also has veins which are probably from the same system. This shows that the veins formed after the assembly of the two blocks.

8. The large quantities of relatively cold sea water passing through the bulk of the Pinbain block, and the hot veins derived from beneath, indicate that there was an active hydrothermal system operating after burial. The heat source for this hydrothermal system is unknown.

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<u>SAMPLE</u>	<u>LITHOLOGY</u>	<u>XRF</u>	<u>PROBE</u>	<u>ISOTOPES</u>	<u>INCLUSIONS</u>
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PREHNITE ZONE

P14A	LAVA	X	X	O,H	
P14B	LAVA				
P15	SAND/SHALE				
P16	LAVA	X	X	O,H	
P20	BRECCIA				X
P21	LAVA			O,H	
P22	LAVA	X	X		

TRANSITON ZONE (SLOCKENRAY BAY)

S1	LAVA	X		O,H	
S2	LAVA	X	X	O,H	
S3	LAVA	X			
S4	LAVA	X	X	O,H	
S5	CONGLOMERATE				
S6	BRECCIA				X
S7	LAVA	X			
S8	LAVA				
S9	LAVA	X			
S10	LAVA	X		H	
S11	LAVA			O	
S12	LAVA		X		
S13	LAVA	X		O	
S14	LAVA	X	X		
S15	BRECCIA			O,H	
S16	AUTOBRECCIA	X			
S17	LAVA	X			
S18	LAVA CLAST				
S19	LAVA CLAST	X			
S20	LAVA CLAST				

ANALCIME ZONE

P23	LAVA	X			
P24	LAVA	X		O,H	
P25	?AUTOBRECCIA				
P26	LAVA	X	X	O,H	
P27	LAVA	X	X		
P28	AUTOBRECCIA				X
P29	BRECCIA	X			
P30	BRECCIA		X	O,H	
P31	BRECCIA				
P32	PILLOW RIM	X		O,H	
P33	LAVA	X			
P34	BRECCIA				
P35	SANDSTONE		X	O,	
P36	BRECCIA				X
P37	LAVA CLAST	X			
P38	SANDSTONE			O,H	
P40	BRECCIA		X	O,H	

KILRANNY CONGLOMERATE

P39A	CONGLOMERATE				
P39B	CONGLOMERATE				

## THE PINBAIN MELANGE

P1	RODINGITIZED GABBRO
P2	LAVA BRECCIA
P3	LAVA BRECCIA
P4	BLACK SHALE
P5	BRECCIATED LAVA
P6	BLACK SHALE
P7	BLACK SHALE. (Probed, and used for fluid inclusion work).
P8	CONGLOMERATE
P9	LAVA
P10	CONGLOMERATE
P11	CONGLOMERATE
P12	BRECCIA
P13	BRECCIA

FELDSPAR

	S2/5F vein	S2/8F	P16/3F vein	P16/8F vein	P16/CF	P30/2F	P14/1F	P14/2F	P14/3F vein
SiO2	61.20	66.12	67.95	66.35	66.30	54.21	69.96	67.65	67.48
TiO2	0.02	0.76	0.03	0.04	0.04	0.13	0.02	0.03	0.04
Al2O3	19.09	19.97	20.13	19.49	19.88	27.03	20.70	20.15	20.46
FeO	0.38	0.73	0.19	0.41	0.00	1.00	0.15	0.09	0.04
MnO	0.00	0.00	0.06	0.02	0.13	0.00	0.00	0.01	0.04
MgO	0.05	0.13	0.02	0.00	0.03	0.03	0.02	0.03	0.00
CaO	0.09	1.21	0.21	0.25	0.91	10.05	0.17	0.16	0.52
Na2O	2.85	11.13	12.70	11.86	10.73	5.07	11.14	10.73	10.94
K2O	12.72	0.10	0.02	0.03	0.06	0.32	0.32	0.05	0.05
P2O5	0.21	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.03
TOTAL	96.97	100.45	101.54	98.71	98.43	98.27	102.68	99.09	99.81
Or%	74.3	0.6	0.1	0.1	0.3	2.0	2.0	0.3	0.3
Ab%	25.3	93.8	99.0	98.9	95.2	46.8	97.3	99.0	97.0
An%	0.4	5.6	0.9	1.0	4.5	51.2	0.8	0.8	2.6

APPENDIX 1.1 FELDSPAR PROBE DATA

FELDSPAR

	P14/4F	P35/3F	P27/5F	P27/6F	P27/7F	P26/CF	P40/2F	P40/3F	P40/4F
SiO2	68.06	67.92	67.79	67.82	67.08	66.65	73.00	67.46	63.78
TiO2	0.03	0.00	0.04	0.00	0.03	0.00	0.37	0.02	1.08
Al2O3	20.47	20.60	20.29	20.82	19.30	20.19	16.38	21.07	18.86
FeO	0.11	0.27	0.13	0.07	0.40	0.52	0.95	0.12	3.18
MnO	0.06	0.00	0.04	0.00	0.02	0.00	0.20	0.00	0.09
MgO	0.00	0.03	0.00	0.00	0.05	0.38	0.00	0.00	1.38
CaO	0.16	0.39	0.11	0.42	0.14	0.17	0.66	0.87	1.94
Na2O	11.02	11.26	11.07	11.95	12.00	11.04	9.00	10.26	9.11
K2O	0.10	0.11	0.10	0.09	0.16	0.07	0.06	0.09	0.08
P2O5	0.00	0.13	0.00	0.03	0.03	0.16	0.26	0.00	1.15
TOTAL	100.23	100.96	99.74	101.45	99.49	99.40	100.94	100.07	100.80
Or%	0.6	0.6	0.6	0.5	0.9	0.4	0.4	0.6	0.5
Ab%	98.6	97.5	98.9	97.6	98.5	98.7	95.7	95.0	89.0
An%	0.8	1.9	0.5	1.9	0.6	0.8	3.9	4.5	10.5

FELDSPAR

	S4/9F vein	S4/AF	S4/BF vein	S4/CFvein	P22/2F	P22/5F
SiO2	64.90	63.78	68.44	69.00	67.39	67.18
TiO2	0.10	0.00	0.01	0.05	0.01	0.03
Al2O3	18.62	19.02	20.40	20.24	20.00	20.46
FeO	0.04	0.05	0.10	0.02	0.69	0.20
MnO	0.00	0.03	0.00	0.07	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.19	0.05
CaO	0.00	0.06	0.43	0.39	0.19	0.44
Na2O	0.13	0.26	10.91	11.56	11.41	10.85
K2O	16.75	15.74	0.10	0.15	0.03	0.29
P2O5	0.00	0.07	0.00	0.02	0.00	0.00
TOTAL	101.00	100.08	100.53	101.75	100.14	99.75
Or%	98.8	97.2	0.6	0.8	0.2	1.7
Ab%	1.1	2.5	97.3	97.4	98.9	96.1
An%	0.0	0.3	2.1	1.8	0.9	2.2

CHLORITE

	S2/7C	S2/9C(V)	P16/1C(V)	P16/2C(V)	P16/4C(V)	P16/5C(V)	P16/6C(V)	P16/7C(V)	P16/9C(V)
SiO2	27.65	28.34	29.96	30.31	25.84	29.36	31.43	27.82	31.58
TiO2	0.01	0.00	0.04	0.04	0.03	0.06	0.00	0.00	0.00
Al2O3	18.17	18.89	16.91	17.65	17.94	15.55	14.50	15.66	16.67
FeO	30.06	28.71	25.86	26.01	33.86	28.17	24.40	29.42	24.59
MnO	0.30	0.43	0.22	0.24	0.43	0.60	0.35	0.41	0.00
MgO	14.82	14.84	14.61	14.40	12.02	12.94	16.83	13.88	12.39
CaO	0.16	0.58	0.41	0.27	0.16	2.12	0.46	0.13	0.69
Na2O	0.00	0.04	0.06	0.06	0.01	0.15	0.11	0.17	0.00
K2O	0.06	0.08	0.07	0.31	0.01	0.05	0.03	0.00	0.68
P2O5	0.00	0.00	0.13	0.12	0.19	0.00	0.03	0.00	0.00
TOTAL	91.38	91.93	88.37	89.62	90.59	89.29	88.33	87.53	86.71
CATIONS									
(14 O)									
Si(IV)	2.86	2.88	3.12	3.11	2.77	3.11	3.26	3.01	3.32
Al(IV)	1.14	1.12	0.88	0.89	1.23	0.89	0.74	0.99	0.68
Al(VI)	1.07	1.15	1.19	1.25	1.04	1.04	1.03	1.01	1.39
Fe	2.60	2.45	2.25	2.23	3.03	2.49	2.11	2.66	2.16
Mg	2.28	2.25	2.27	2.20	1.92	2.04	2.60	2.24	1.94

APPENDIX 1.2 CHLORITE PROBE DATA

(V) = vein occurrence  
 (P) = Alteration of Chlorite  
 (F) = " " Feldspar

CHLORITE

	P16/AC	P16/BC	P30/1C(v)	P30/3C	P30/4C	P30/5C	P14/6C	P14/7C	P14/8C
SiO2	29.84	29.76	31.59	35.18	31.67	37.76	24.95	25.00	34.29
TiO2	0.00	0.05	0.01	0.00	0.00	0.16	0.03	0.00	0.00
Al2O3	17.59	17.94	12.78	11.85	12.34	15.84	17.00	16.04	14.30
FeO	26.59	26.39	26.72	27.51	25.14	20.01	38.29	37.86	20.74
MnO	0.26	0.19	0.24	0.24	0.02	0.00	0.47	0.48	0.20
MgO	12.98	13.86	17.15	14.68	17.75	18.93	8.31	8.01	18.83
CaO	0.33	0.29	0.40	0.25	0.35	0.72	0.26	0.22	0.90
Na2O	0.00	0.00	0.00	0.08	0.00	0.04	0.09	0.15	0.06
K2O	0.14	0.19	0.00	0.08	0.07	0.15	0.00	0.03	0.02
P2O5	0.13	0.01	0.12	0.00	0.00	0.12	0.09	0.00	0.00
TOTAL	87.99	88.80	89.18	90.02	87.54	93.98	89.64	88.01	89.46
Si(IV)	3.12	3.09	3.28	3.60	3.33	3.53	2.79	2.84	3.42
Al(IV)	0.88	0.91	0.72	0.40	0.67	0.47	1.21	1.16	0.58
Al(VI)	1.29	1.29	1.57	1.03	0.86	1.26	1.03	1.00	1.10
Fe	2.36	2.29	2.32	2.35	2.21	1.56	3.57	3.60	1.72
Mg	2.02	2.14	2.65	2.23	2.78	2.63	1.38	1.36	2.79

CHLORITE

	P35/2C	P27/1C(V)	P27/3C	P26/2C(X)	P26/5C	P26/6C(f)	P26/8C(V)	P26/AC(F)	P40/5C
SiO2	25.52	30.63	30.03	31.62	27.04	30.30	34.40	32.11	31.14
TiO2	0.04	0.00	0.04	0.00	0.62	0.01	0.00	0.00	0.00
Al2O3	16.25	12.52	13.34	16.44	14.66	16.07	15.79	15.75	14.27
FeO	30.64	22.72	22.43	22.41	28.77	23.44	21.94	21.60	26.61
MnO	0.27	0.36	0.21	0.35	0.14	0.41	0.34	0.41	0.19
MgO	11.52	17.66	17.54	20.45	17.68	19.23	15.78	18.85	16.01
CaO	0.17	0.76	0.44	0.42	0.73	0.28	0.43	0.62	0.41
Na2O	0.07	0.00	0.04	0.18	0.08	0.01	2.41	0.00	0.02
K2O	0.03	0.08	0.03	0.07	0.01	0.05	0.01	0.03	0.00
P2O5	0.00	0.00	0.19	0.00	0.00	0.14	0.02	0.00	0.00
TOTAL	84.56	85.30	84.49	91.98	89.79	90.04	91.16	89.46	88.77
Si(IV)	2.90	3.29	3.23	3.11	2.86	3.07	3.40	3.22	3.25
Al(IV)	1.10	0.71	0.77	0.89	1.14	0.93	0.60	0.78	0.75
Al(VI)	1.08	0.87	0.93	1.01	0.69	0.98	1.24	1.08	1.00
Fe	2.91	2.04	2.02	1.84	2.54	1.98	1.81	1.81	2.32
Mg	1.95	2.83	2.82	2.99	2.78	2.90	2.32	2.82	2.48

CHLORITE

	P407C	S14/3C(px)	S14/8C	S12/1C(v)	S12/4C(v)	S12/5C(px)	S12/7C(v)	S4/1C	P22/3C(v)
SiO2	32.10	36.33	33.67	39.81	31.62	33.85	33.79	31.75	28.30
TiO2	0.01	0.00	0.00	0.07	0.00	0.00	0.03	0.02	0.07
Al2O3	14.93	14.19	13.53	15.67	11.99	12.77	11.91	14.50	18.71
FeO	25.42	17.58	17.22	17.13	23.12	23.84	22.58	29.12	29.21
MnO	0.31	0.17	0.27	0.21	0.51	0.35	0.06	0.39	0.27
MgO	17.91	22.24	20.32	13.48	17.34	17.96	14.70	14.23	14.99
CaO	0.46	1.08	0.97	0.90	1.20	1.13	1.37	1.11	0.25
Na2O	0.12	0.10	0.03	0.76	0.17	0.08	0.15	0.11	0.00
K2O	0.03	0.01	0.01	0.09	0.13	0.08	0.20	0.03	0.00
P2O5	0.05	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.17
TOTAL	91.57	91.98	86.40	88.33	86.23	90.15	84.87	91.35	92.19
Si(IV)	3.22	3.46	3.42	3.88	3.36	3.42	3.60	3.26	2.88
Al(IV)	0.78	0.54	0.58	0.12	0.64	0.58	0.40	0.74	1.12
Al(VI)	0.98	1.05	1.04	1.67	0.86	0.94	1.10	1.01	1.12
Fe	2.13	1.40	1.46	1.39	2.05	2.01	2.01	2.50	2.48
Mg	2.67	3.15	3.07	1.95	2.75	2.70	2.33	2.17	2.27

	S2/4A	S2/6A	P26/1A	P26/3A	P26/7A	P26/9A	P26/8A
SiO2	54.86	54.62	57.02	54.97	54.97	55.49	58.25
TiO2	0.00	0.00	0.05	0.00	0.00	0.00	0.11
Al2O3	22.06	21.27	23.23	22.26	22.32	22.66	23.95
FeO	0.05	0.67	0.03	0.15	0.02	0.05	0.25
MnO	0.00	0.10	0.07	0.00	0.00	0.00	0.00
MgO	0.00	0.20	0.00	0.07	0.00	0.05	0.04
CaO	0.86	0.01	0.04	0.02	0.04	0.04	0.11
Na2O	12.37	12.96	10.74	11.44	11.90	12.19	9.85
K2O	0.07	0.02	0.02	0.06	0.01	0.02	0.06
P2O5	0.00	0.00	0.00	0.06	0.05	0.02	0.00
TOTAL	90.40	89.95	91.28	89.48	89.48	90.75	92.88
CATIONS (7 O)							
Si	1.98	1.97	2.05	1.96	1.96	2.00	2.11
Al	0.94	0.90	0.98	0.93	0.94	0.96	1.02
Na	0.87	0.91	0.75	0.79	0.82	0.85	0.69

APPENDIX 1-3 ANALCIME PROBE DATA

SPHENE

	S2/3S	P14/5S	P40/6S	S12/3S
SiO2	27.23	35.97	37.17	31.66
TiO2	30.54	24.28	25.70	31.97
Al2O3	5.02	7.84	6.22	3.17
FeO	6.48	1.31	2.97	2.54
MnO	1.04	0.00	0.00	0.00
MgO	1.41	0.37	0.39	0.24
CaO	23.44	21.38	21.83	26.64
Na2O	0.00	0.03	2.06	0.09
K2O	0.00	3.03	0.05	0.09
P2O5	2.00	0.03	0.74	0.03
TOTAL	98.47	95.11	98.01	97.46

APPENDIX 1-4 SPHENE PROBE DATA

## Analytical conditions

Element	Line	Background	Time(s)	Crystal	Counter	Coll.	KV	mA
Si	K-alpha	-2.20	40	PE	Flow	C	50	32
Ti	K-alpha		20	LiF200	Flow	C	60	24
Al	K-alpha		40	PE	Flow	C	60	32
Fe	K-alpha		20	LiF200	Flow	C	60	24
Mn	K-alpha	+2.85	100	LiF200	Flow	C	60	32
Mg	K-alpha	+2.68	100	TAP	Flow	C	60	32
Ca	K-alpha		20	LiF200	Flow	C	60	24
Na	K-alpha	-2.25	100	TAP	Flow	C	60	32
K	K-alpha		40	PE	Flow	C	60	32
P	K-alpha	+1.93	100	PE	Flow	C	60	32
Nb	K-alpha	+2.88	100	LiF200	Scint	F	60	32
Zr	K-alpha	-1.55	100	LiF200	Scint	C	60	32
Y	K-alpha	+0.48	100	LiF200	Scint	C	60	32
Sr	K-alpha	+1.17	100	LiF200	Scint	C	60	32
Rb	K-alpha	+0.58	100	LiF200	Scint	C	60	32
Pb	L-beta(1)	+0.54	100	LiF200	Scint	F	60	32
Th	L-alpha(1)	-0.23	100	LiF200	Scint	F	60	32
Mn	K-alpha	+1.28	40	LiF220	Flow	C	60	32
V	K-alpha	-2.60	100	LiF220	Flow	F	60	32
Ba	L-beta(1)	+1.80	100	LiF220	Flow	F	60	32
Hf	L-alpha(1)	+1.00	100	LiF200	Flow	F	60	32
Ce	L-beta(1)	-0.90	100	LiF200	Flow	F	60	32
La	L-alpha(1)	+2.70	100	LiF220	Flow	C	60	32
Ti	K-beta(1+2)		20	LiF220	Flow	F	60	32
Zn	K-alpha	-1.27	40	LiF220	Flow	C	60	32
Cu	K-alpha	+1.84	20	LiF200	Flow	C	60	32
Ni	K-alpha	+1.30	40	LiF200	Flow	C	60	32
Cr	K-alpha	+1.40	20	LiF200	Flow	C	60	32

Sample	P14A	P16	P22	S1	S2	S3
SiO2	57.53	53.54	49.77	42.26	46.22	49.27
TiO2	0.83	0.80	1.49	1.53	1.44	2.23
Al2O3	17.92	19.14	18.07	20.02	19.55	13.89
Fe2O3	6.26	8.46	8.27	7.26	7.43	12.80
FeO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.11	0.14	0.14	0.13	0.16	0.18
MgO	1.69	2.85	3.07	3.16	3.99	5.23
CaO	3.92	2.89	8.48	18.16	11.02	6.71
Na2O	8.60	7.10	5.93	2.51	4.19	5.65
K2O	1.47	0.94	0.15	0.20	0.52	0.13
P2O5	0.50	0.28	0.27	0.31	0.20	0.33
Loss	1.40	2.60	4.15	5.60	5.80	3.80
<b>TOTAL</b>	<b>100.31</b>	<b>98.89</b>	<b>99.88</b>	<b>101.22</b>	<b>100.61</b>	<b>100.32</b>
Nb	0	0	0	2	0	0
Zr	118	92	111	106	103	165
Y	35	20	23	25	22	29
Sr	145	343	134	60	117	170
Rb	10	14	4	5	10	4
Th	9	7	0	0	3	0
Pb	24	11	0	1	5	8
Zn	137	78	91	80	80	109
Cu	50	215	91	49	72	83
Ni	11	16	44	54	45	21
Cr	0	9	82	78	79	6
V	59	293	283	327	297	380
Ba	119	303	31	10	40	54
Hf	3	3	2	2	2	2
Ce	84	60	34	12	28	12
La	31	15	6	0	0	0

Sample	S4	S7	S9	S17	S19	S10
SiO2	49.97	47.83	50.79	50.08	52.47	45.33
TiO2	1.35	1.51	1.54	2.31	2.27	2.21
Al2O3	16.65	19.26	16.89	13.73	14.84	19.26
Fe2O3	7.29	7.53	10.14	11.72	9.50	10.68
FeO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.14	0.13	0.18	0.20	0.19	0.17
MgO	3.26	2.72	5.42	5.03	3.57	5.45
CaO	8.35	9.38	4.61	6.82	9.26	4.56
Na2O	5.59	6.07	5.77	6.56	3.69	4.64
K2O	2.77	0.83	1.40	0.49	0.96	2.02
P2O5	0.21	0.26	0.22	0.35	0.36	0.31
Loss	5.20	4.90	3.40	2.73	4.40	4.00
TOTAL	100.97	100.58	100.51	100.14	101.63	98.78
Nb	1	2	0	5	3	5
Zr	105	115	115	180	189	154
Y	18	24	24	30	31	25
Sr	528	426	425	287	384	278
Rb	29	9	17	9	14	19
Th	0	0	0	2	1	0
Pb	1	4	4	1	4	2
Zn	66	77	68	82	82	85
Cu	67	71	68	86	86	35
Ni	40	45	59	40	35	34
Cr	58	81	100	28	0	31
V	253	271	267	352	281	297
Ba	709	398	276	51	78	502
Hf	5	10	3	3	4	3
Ce	6	39	49	64	41	29
La	0	0	0	0	0	0

Sample	S13	S14	S16	P23	P24	P26
SiO2	48.92	50.44	45.88	48.82	49.11	47.06
TiO2	1.85	2.05	2.15	1.84	2.28	1.84
Al2O3	16.76	15.03	16.82	17.34	14.29	16.99
Fe2O3	10.19	10.68	10.67	9.66	10.77	9.09
FeO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.17	0.16	0.20	0.16	0.25	0.14
MgO	6.09	5.47	6.64	5.75	7.10	6.14
CaO	5.57	5.01	5.23	6.29	7.23	4.52
Na2O	5.27	6.37	4.21	5.53	4.72	7.86
K2O	0.98	0.94	1.61	0.54	1.01	0.69
P2O5	0.26	0.27	0.30	0.25	0.32	0.27
Loss	4.60	3.87	7.00	4.60	3.10	6.80
TOTAL	100.82	100.39	100.84	100.92	100.34	101.51
Nb	5	5	5	3	5	3
Zr	150	156	166	144	169	139
Y	25	25	26	23	28	22
Sr	563	134	275	592	452	188
Rb	8	7	14	8	11	9
Th	1	2	0	0	0	1
Pb	2	6	5	7	2	4
Zn	80	75	83	76	92	87
Cu	65	77	67	62	72	126
Ni	56	45	50	57	55	59
Cr	43	10	51	29	68	55
V	266	270	331	267	342	258
Ba	283	147	204	127	205	189
Hf	3	4	3	4	3	3
Ce	32	69	40	26	57	6
La	2	3	3	0	0	0

Sample	P27	P29	P32	P33	P37
SiO2	58.71	55.99	50.16	46.78	51.02
TiO2	0.95	2.54	1.86	1.63	2.09
Al2O3	17.03	14.56	18.96	19.02	17.12
Fe2O3	5.53	13.25	6.72	7.34	11.11
FeO	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.09	0.09	0.12	0.14	0.14
MgO	2.48	2.27	5.03	4.84	5.07
CaO	2.21	1.89	4.78	6.51	2.67
Na2O	9.46	6.21	6.18	5.58	7.23
K2O	0.68	1.36	0.76	0.88	0.51
P2O5	0.18	0.39	0.31	0.23	0.34
Loss	2.70	1.60	5.80	6.20	3.80
TOTAL	100.08	100.26	100.83	99.29	101.22
Nb	0	8	2	0	4
Zr	150	273	143	121	158
Y	34	36	32	23	28
Sr	116	222	355	265	334
Rb	5	21	11	13	10
Th	0	0	0	0	0
Pb	4	4	7	10	3
Zn	90	85	94	81	149
Cu	28	10	125	74	44
Ni	8	13	62	47	21
Cr	0	0	113	88	12
V	135	289	343	298	303
Ba	18	60	150	301	65
Hf	4	4	3	4	4
Ce	36	68	42	26	22
La	0	0	8	2	3