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Holocene environmental and pedogenic history of the Hiraethog Moors, Clwyd

Lascelles, D.Bruce

Award date:
1995

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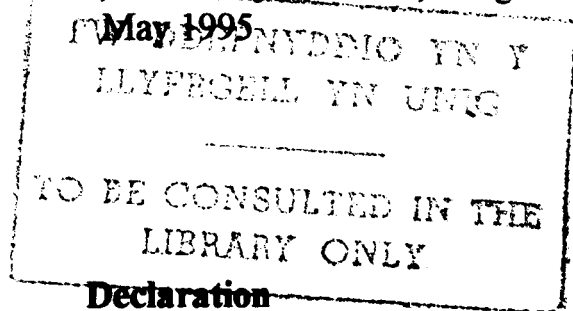
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Holocene environmental and pedogenic history of the Hiraethog Moors, Clwyd.

by

D.B. Lascelles

A thesis presented for the degree of Ph.D from the School of Agricultural and Forest Sciences, University of Wales, Bangor.



I hereby declare that the work in this thesis has not previously been accepted for any degree and is not concurrently submitted for any other degree.

The experimental work described in this thesis was carried out by myself in the School of Agricultural and Forest Sciences, University of Wales, Bangor under the direction of Dr. D.A. Jenkins.

Candidate.....**D.B. Lascelles**
Director of studies.....**Dr. D.A. Jenkins**
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Summary

This project describes the Holocene environmental and pedogenic history of the Hiraethog Moors, particularly in relation to archaeological evidence.

Ironpan stagnopodzol, brown podzolic and stagnohumic gley profiles have been studied from Aled Isaf together with cores from Cefn Mawr and Llyn y Foel-frech. Physical, chemical, clay mineralogical, micromorphological and palynological analyses have been undertaken and a time framework has been achieved by radiocarbon dating, including AMS ^{14}C dating of ironpan and charcoal samples. A search for tephra has been undertaken and, although none was located, the presence of a biolith bloom in a core from Llyn Cororion on the Arfon Platform raises the possibility of a geochemical reconstitution of a low volume, fine-grained tephra fall.

Parent material was reworked by periglacial processes during the Late-glacial resulting in an oriented fabric, cracked stones and a redistribution of clay and fine silt-sized material. Until 6-7,000 years BP soils remained shallow and stony, with a clay mineralogy dominated by hydrous mica and chlorite. Between 6,000 and 4,000 years BP erosion led to deeper soil profiles on the lower slopes, burying flints and charcoal, and the woodland was periodically disturbed by humans. However, man was relatively inactive between 4,500 and 3,500 years BP.

At 3,500 years BP woodland cover declined rapidly due to human activity with a subsequent change to a Gramineae- and then a *Calluna*-dominated vegetation community. In low lying sites the result was increased waterlogging, gleying, structural collapse and the build up of organic matter at the surface *i.e.* stagnohumic gley. In better drained sites podzolisation occurred to produce the B_s horizon, *i.e.* brown podzolic soil. In profiles most intensively leached, mor humus and then peat accumulated. This induced surface waterlogging resulting in a mobilisation of iron, structural collapse and the formation of an E_{ag} horizon, within which chlorite was destroyed and hydrous mica weathered to vermiculite, and an ironpan *i.e.* ironpan stagnopodzol.

Through the integration of soil and pollen analysis, ^{14}C dating and archaeological information our understanding of soil development and human activity on Hiraethog has been increased.

Acknowledgements

I wish firstly to thank the School of Agricultural and Forest Sciences for funding this work through a Studentship grant, and NERC Scientific Services for technical and financial support in respect of the radiocarbon dating undertaken. I would like to express gratitude to my supervisor, Dr David Jenkins, for his kindness and constant advice and encouragement throughout this project, and for his unending supply of new thoughts and ideas with which to toy. I would also like to thank Dr James Scourse for allowing me access to his pollen laboratory and reference collection, and for his help and advice on pollen-related problems.

Thanks must also be given to a number of people who have provided me with advice, access to facilities and help with the tasks that I undertook, including friends and colleagues in the School of Agricultural and Forest Sciences, particularly I. Kelso, A. Owen and B. Girmay in Soil Science, for advice, help and encouragement over the years; S. Whalley from the School of Ocean Sciences (SOS) for assistance with fieldwork and for acting as a sounding board for new ideas; A. Nield (SOS) for help with coring. To A. Davies for support with SEM work and to Dr R. Oxley for guidance with GIS techniques. I would particularly like to thank Hilton Trow for his kindness and tireless assistance in both the laboratory and the field. Finally I would like to thank friends and family who have supported me physically and financially (respectively) throughout my stay in Bangor.

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Chapter 1. Introduction

Although there is archaeological evidence for Mesolithic and Bronze Age human activity at upland sites in Clwyd, such as Brenig and Aled Isaf on the Hiraethog Moors (see figures 2.1 and 2.7 for locations), this information stands in relative isolation. It has been suggested (Jenkins, 1991) that "a proper understanding of man's history in Clwyd can only come with the continued accumulation of information from detailed, multidisciplinary studies". This project aimed to study the Holocene environmental history of Hiraethog, in terms of pedogenesis and vegetation change, to facilitate the understanding of such processes *per se* and to aid interpretations of human activity in this area.

The Aled Isaf reservoir and surrounding moorland was chosen as the study site for several reasons:

1. the soils exposed are characteristic of many other upland areas, such as mid-Wales and the Southern Uplands of Scotland, and therefore the results would have much wider relevance;
2. there is an abundance of natural peat bogs and lakes from which sediment cores for microfossil analyses could be recovered;
3. across the Hiraethog Moors archaeological remains have been found, and it was of interest to study the interaction of man with the environment, particularly in terms of soil development.

Chapter 2 describes the Hiraethog Moors in terms of its landscape, geology, climate and soils, as well as its glacial and archaeological Quaternary history. The soils found over the Hiraethog Moors, particularly the stagnohumic gleys, ironpan stagnopodzols and brown podzolic soils, have been studied in detail in the past in terms of their mineralogy (Livesey, 1966; Lewis, 1970; Bower, 1970; Rezk, 1975), their physical and chemical properties (Ball, 1960; Avery, 1990) and their moisture regimes (McHugh, 1989). However, no overall analysis has been carried out into the sequence of events which may have led to their formation, or into the environmental conditions which have prevailed on Hiraethog during the Holocene period.

Human activity on Hiraethog since the mid-Holocene has been inferred from archaeological evidence, but there is a lack of information available concerning the environment in which people were living and the impact on the environment which their actions had. Hiraethog is a typical upland area with a vegetation community dominated

by acidophile species such as *Calluna* and *Molinia*, and the characteristic soils as outlined above. Soils are continually evolving in response to changing environmental conditions and this project aimed to look at the interrelationships between pedogenesis and various environmental parameters to build up an overall environmental history of the Hiraethog Moors, which in general terms will be applicable to other upland regions of the U.K..

In order to improve our understanding of the processes involved a multidisciplinary approach was used to tackle the problem, with the aim of:

1. defining present-day soil characteristics;
2. studying past pedogenic activity and processes;
3. studying vegetation change across Hiraethog during the Holocene;
4. placing vegetation (and therefore environmental?) and pedogenic changes in a relative or absolute time framework;
5. relating such changes to known human activity on the Moors.

Chapter 3 reviews the literature concerning the soil types, their chemical and physical properties, clay mineralogy and micromorphological characteristics, and outlines some of the views held concerning the pedogenic processes which are thought to have occurred to result in the characteristic soil profiles seen today. Present-day soil characteristics have been elucidated by studying soil physical and chemical properties, the mineralogy of the clay fraction and the morphology of the soils, both on a macro- and micro-scale, so allowing comparisons to be made with existing research in the literature. These data have also been used in an attempt to make interpretations about past phases of pedogenic activity. All these techniques allow the parent material to be characterised, and when this is compared with overlying horizons it provides information about the changes that have occurred over time in the soils. By studying three different soil series has allowed the influence of factors such as relief to be determined since all profiles were formed in similar parent material and under a similar climate at the same altitude.

Hiraethog is thought (Avery, 1990) to have been dominated by brown earth soils during the climatic optimum and that the influence of differing site conditions, particularly relief and vegetation, led to the strikingly different profile morphologies seen today. Of particular interest, and a central theme to this project, are the processes leading to and the timing of the formation of ironpans in the stagnopodzolic profiles. The hypothesis generally accepted for their formation is that a change in the vegetation community, occasioned by climatic change or human activity, resulted in the build up of peat at the

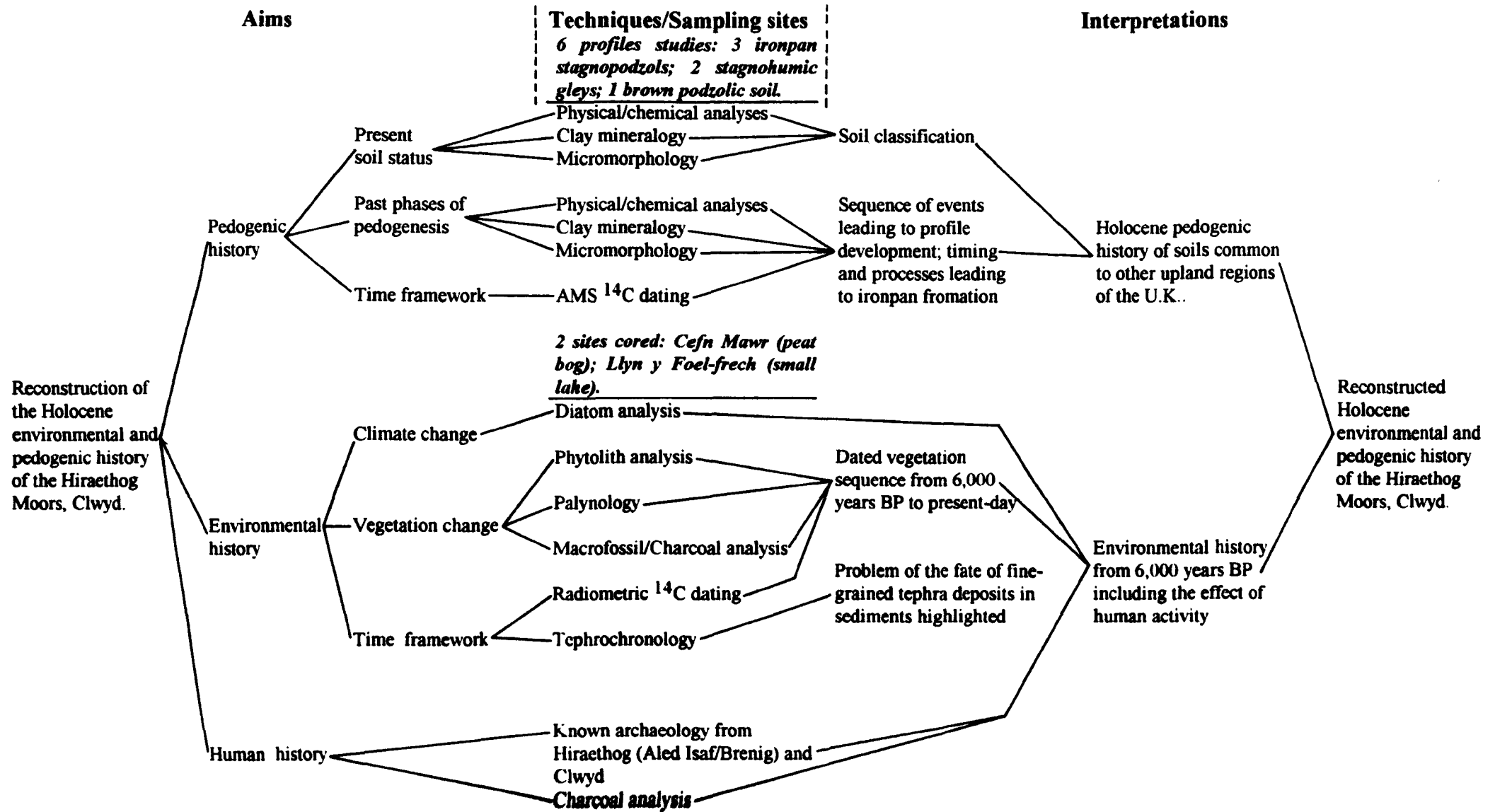
surface of the mineral soil. This is thought to have led to surface gleying and a redistribution of iron as an ironpan horizon (Avery, 1990).

The resolution of the sequence of events that occurred and the time frame involved required the use of several techniques, including clay mineralogy, micromorphology and radiocarbon dating. AMS ^{14}C dating, with its small carbon requirement, was employed here in an attempt to accurately date the age of the ironpans. This has been a novel use of AMS ^{14}C dating and a new approach to understanding the sequence of events which have occurred in these soils. Only one study had previously been undertaken concerning the exact timing of the formation of ironpans, as outlined in Avery (1990), and the conclusions drawn from this present study are of great interest and value but also highlight the need for further detailed analyses to be undertaken. This has also allowed pedogenic processes to be related to specific phases of vegetation change on Hiraethog and so to be interpreted in the light of this information. The time of formation of an ironpan is of obvious interest to pedologists but is also of value in archaeological investigations since an ironpan may extend over a wide area and may pass through one or more archaeological points of interest; knowledge of the age of the ironpan would therefore facilitate interpretations made concerning the archaeological features.

Chapter 4 reviews the literature concerning the general patterns of vegetation change that have occurred in Britain over the Holocene, with more detailed discussions of those changes which are thought to have more direct relevance to this project and Hiraethog such as the elm decline and the initiation of peat in many of the upland regions, both usually inferred to be a result of human interference in the environment. The alder rise is also discussed since it was initially thought possible that this was represented at the base of the peat core recovered relating to around 8,000 years BP when the alder rise is recorded at other sites in North Wales. Palynology was the main process used in the reconstruction of vegetation changes with additional information on possible human activity coming from an analysis of the charcoal preserved in the peat core. Bioliths and plant macrofossils were tentatively analysed and whilst it was clear that both could supply further valuable information time constraints dictated that neither could be pursued to a greater extent.

A time framework for the vegetation changes noted was supplied by radiocarbon dating (radiometric) allowing integration of this information with pedogenic and archaeological events for Hiraethog. The value of tephrochronology as a dating process is clearly exemplified in other studies and was hoped to be utilised in this project to provide one or more isochronous marker horizons for inter-site correlation. However since no tephra

Summary of aims, objectives, techniques employed and interpretations made



could be located in an initial study of sediments from North Wales, again this avenue of research could not be followed further. However, the absence of tephra itself raised certain interesting questions which have yet to be answered.

The final chapter attempts to describe the vegetation and environmental changes established for Hiraethog over the last 6,000 years and to link these with the pedogenic processes which were thought to have produced its soils. It is believed that this thesis provides at least partial answers to the following:

1. what were the vegetation changes on Hiraethog during the Holocene and what impact did man have on this vegetation during this time?
2. what pedogenic processes have influenced soils of the Hiraethog Moors, and in what sequence did they occur, particularly in relation to the formation of the ironpan in the present-day ironpan stagnopodzolic profiles?
3. how vegetation change, determined by man or otherwise, has affected pedogenic processes and therefore the soil characteristics observed at the present-day?

With the range of techniques used final conclusions from any one are in places tentative. However, in attempting to piece together the environmental history of an area the integration of data from several disciplines does provide a clearer picture than more detailed data from just one discipline could. To further improve our understanding of the interrelationships between vegetation, soil and man over time there is clearly a need for more such multidisciplinary studies to be undertaken.

Chapter 2. Description of the area and environment of the Hiraethog Moors.

2.1 Study area

This work was carried out in North Wales, in the region centred around the Aled Isaf Reservoir on the Hiraethog Moors, an area of about 175km², not including Clocaenog forest, in the county of Clwyd. The land rises to around 430m above sea level, lying to the south-east of the main mountain range of Snowdonia. The geographical position and the location of all the sites studied is shown in fig.2.1. The region does not have as diverse an environment as the mountains of North Wales due to more uniform geology and topography, the main aspects of which are discussed below.

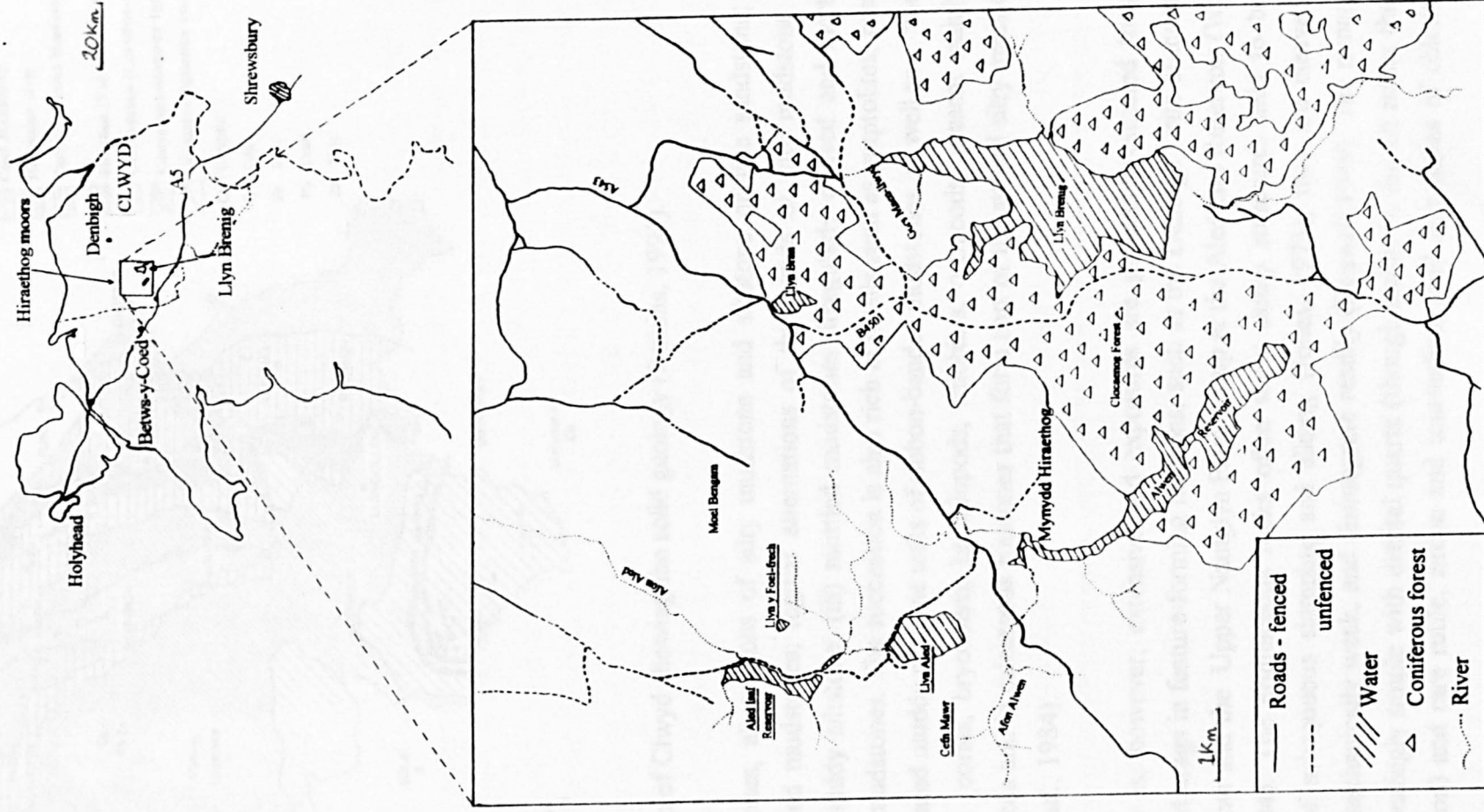
2.2 Geology

Within Clwyd four physical regions have been defined by Ball (1960) which are controlled by the under-lying geology; the Denbigh uplands and moors; the limestone ridge and coastal fringe; the Vale of Clwyd and the Clwydian Hills. This study focused on the Denbigh uplands and moorlands, since it is in this region that the archaeological artefacts and soil exposures, which were of interest to this particular line of research, were found. Fig. 2.2 shows a map of the solid geology (Jenkins,1991) in which the four areas outlined above can be distinguished.

The study area around Mynydd Hiraethog is comprised of a relatively simple solid geology, described by Warren *et al.* (1984) as consisting mainly of mildly deformed Silurian sedimentary rocks of Wenlock and Ludlow age (greywacke facies) with no known volcanic or intrusive igneous rocks, although there is sporadic Pb, Cu and Zn mineralisation. The total outcrop covers about 550km², extending from the high ground of the Denbigh Moors to sea-level at the coast, and is presumed to extend at depth beneath the Carboniferous and Permo-Triassic outcrops to the north and east (Warren *et al.*, 1984).

The sedimentary rocks are essentially non-calcareous comprising mainly shales, mudstones and siltstones with occasional gritstone bands and conglomerates. Warren *et al.* (1984) subdivide the finer grained sediments into three groups: (i) striped

Figure 2.1 Location map of the Hiraethog Moors and sampling sites (underlined).



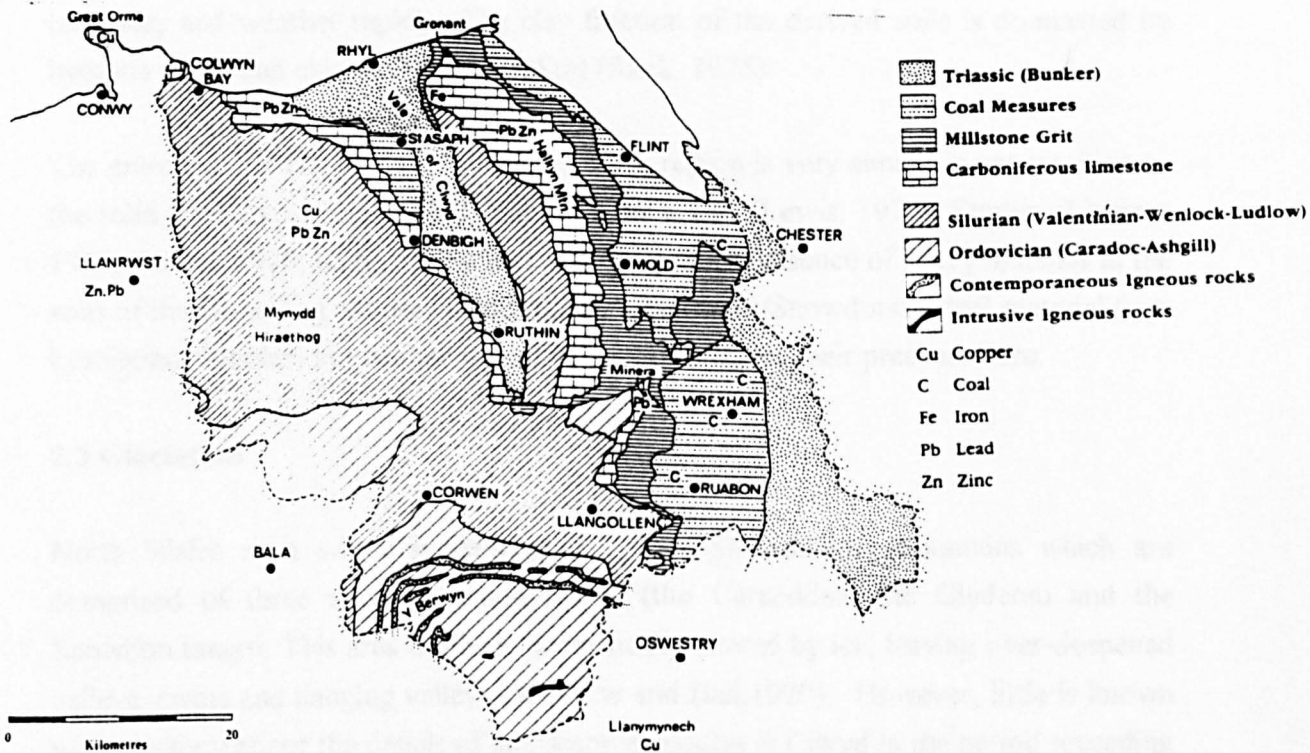


Fig. 2.2 Map of Clwyd showing the solid geology (Jenkins, 1991).

silty mudstones; alternations of silty mudstone and siltstone or fine sandstone; (ii) ribbon-banded mudstones; regular alternations of thin bands of silty mudstone and laminated muddy siltstone; (iii) mottled mudstones; irregularly cleaved and mottled, calcareous mudstones. The succession is also rich in fossils such as graptolites, present in the laminated muddy siltstone units of ribbon-banded mudstones, as well as a "shelly" macrofauna (corals, bryozoans, brachiopods, trilobites, ostracods) present mainly in disturbed beds and in calcareous siltstones that form part of the striped silty mudstones (Warren *et al.*, 1984).

Drift cover is, however, extensive and exposures are generally restricted to small quarries and crags in feature-forming horizons, such as the Denbigh Grits outcropping at Cefn Mawr and the Upper Nantglyn Flags group at the Aled Isaf Reservoir (Warren *et al.*, 1984). The argillaceous rocks often show slump structures held to be the products of subaqueous slumping and sliding (Jones, 1973); they are cleaved and therefore mechanically weak, and disintegrate readily (Boswell, 1949). The mineralogy is correspondingly simple with detrital quartz (though mainly in the silt rather than the sand fraction) and rare rutile, zircon and tourmaline; sand size flakes of chlorite are

common, and weather rapidly. The clay fraction of the derived soils is dominated by hydrous micas and chlorite (\pm vermiculite) (Rezk, 1975).

The extensive covering of drift material in this region is very similar in composition to the solid geology, simply eroded rocks of local origin (Lewis, 1970). Studies (Livesey, 1966; Bower, 1970; Rezk, 1975) have shown the rare presence of heavy minerals in the soils of the Hiraethog Moors characteristic of Northern/Snowdonian drift material (*e.g.* kyanite/amphiboles) but aeolian transport is suggested for their presence here.

2.3 Glaciation

North Wales as a whole is dominated by the Snowdonian Mountains which are comprised of three main mountain ridges (the Carneddau, the Glyderau and the Snowdon range). This area has been dramatically altered by ice, leaving over-deepened valleys, cwms and hanging valleys (Whittow and Ball, 1970). However, little is known with certainty about the details of landscape evolution in Clwyd in the period preceding the Quaternary glaciations. In a review of the evidence put forward by other workers, Derbyshire (1993) suggested that Mynydd Hiraethog represented a remnant of an erosion surface ("Middle Peneplain") of early Tertiary age, with high points standing above it, such as Mwdwl Eithin, being residual remnants of an even higher surface of peneplain type. Certainly the surface centred on Mynydd Hiraethog cuts discordantly across the folded structure of the Silurian rocks, but Derbyshire (1993) concluded that the nature of the erosive agent - river planation, glacial erosion or atmospheric weathering - has yet to be determined. Derbyshire (1993) suggested that the drainage may have originated on an easterly tilted surface of Cretaceous rocks which were later stripped off, the drainage becoming superimposed and cutting a succession of partial peneplains on the Silurian rocks. However, since no remnants of Cretaceous, Jurassic or Triassic rocks have been found on this surface, and as none of the erosion surfaces appear to be warped, he suggested that the process itself, or the rate of the process, must be left in question.

Mynydd Hiraethog lacks the spectacular glacial scenery of Snowdonia, and there is little evidence of striations on any of the outcrops to reconstruct ice movement since Silurian mudstones are unsuited to the preservation of such features.

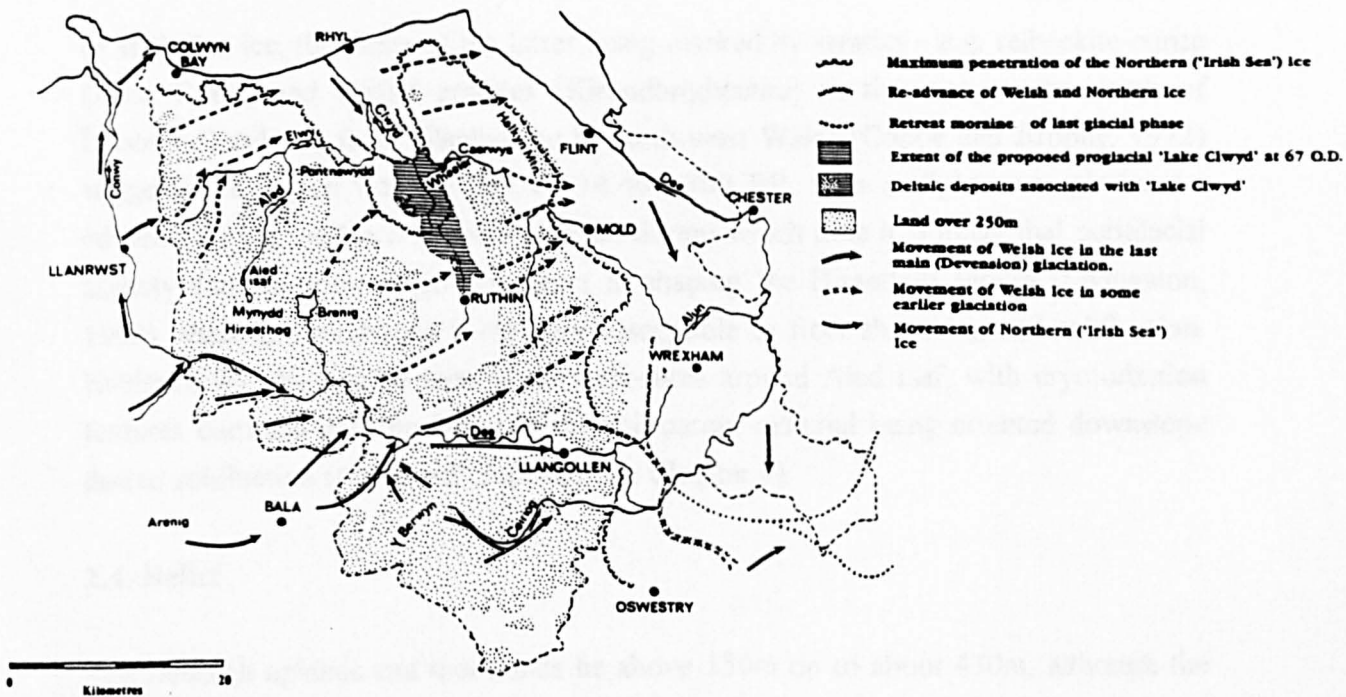


Figure 2.3 Selected features of the Quaternary in Clwyd (Jenkins, 1991).

However the overall movement and origins of ice which has affected Mynydd Hiraethog has been deduced from the landforms and stratigraphy of the area between the fault scarp of the Clwydian Hills and the glacial trough of the Vale of Conwy, and from such evidence Livingston (1990; 1991) described three phases of glaciation in Clwyd, details of which are presented in figure 2.3 (Jenkins, 1991). She cites the erratic lithology and heavy mineral suites of deposits dated to before 225,000 years BP in Pontnewydd Cave as evidence for "early" glaciation of the area by an advance of an Irish Sea ice mass, which may also have diverted the course of the Elwy between Ddol and Cefn Rocks, and suggested that this related to the Beestonian Northern Drift Glaciation or the even earlier Baventian cold stage (Oxygen Isotope Stage >12). The second phase described by Livingston (1991) is thought to relate to a period when an extensive Welsh Ice Sheet prevented Northern ice from penetrating inland, causing it to pile up against the coastal hills, leaving Irish Sea tills at heights of between 300m O.D. (Moel y Crio) and 580m O.D. (Moel Wnion and Moel Tryfan).

Livingston (1990) divided the final event into two phases, one post 30ka and one post 18ka. The first is thought to have involved Irish Sea and Welsh Ice following roughly the same flow patterns as before, the second an Irish Sea ice re-advance with the possibility of a Denbigh Moors ice cap forming, preventing inundation by either Welsh

or Irish Sea ice, the limits of the latter being marked by erratics - *e.g.* reibeckite-urite (Ailsa Craig) and Criffel granites (Kirkudbrightshire) in the area to the north of Denbigh. Evidence from Glanllynau in north-west Wales (Coope and Brophy, 1972) suggests the region was ice free by $14,468 \pm 300$ BP, with a slight cwm glacier re-advance during the Loch Lomond stadial, during which time it is likely that periglacial activity was the most important agent in shaping the Hiraethog Moors (Livingston, 1990), shale and mudstone being very susceptible to frost-shattering and solifluction. Evidence for this can be seen in the exposures around Aled Isaf, with cryoturbation features common and the fabric of the soil parent material being oriented downslope due to solifluction (*i.e.* "head" deposits, see Chapter 6).

2.4. Relief

The Denbigh uplands and moorlands lie above 150m up to about 430m, although the highest point near Llyn Brân lies at about 520m. The area is much dissected, with hill blocks separated by narrow, steep-sided, flat-floored valleys, the blocks often so dissected that individual hills and ridges are formed (Challinor & Bates, 1973). The Elwy drains the major part of the uplands and, with its tributaries the Gallen, Cledwen and Aled, has its source in the moorland near Mynydd Hiraethog.

The main study area is the reservoir Aled Isaf, which was built in the 1930s. Water storage is within a shallow river valley, the dam lying slightly upstream from a waterfall and gorge that the river subsequently enters. The topography of the valley is shown in figure 2.4., a 3-D model built up using a contour map produced by the Dee and Clwyd Water Authority prior to the valley being flooded.

2.5. Climate

The present-day climate of this area and of N. Wales as a whole is typically maritime, with the humidity being generally high, and minimum winter temperatures on average a few degrees higher and maximum summer temperatures a few degrees lower than those of the south-east of the British Isles (Ball, 1960). In this region rainfall is lowest in the

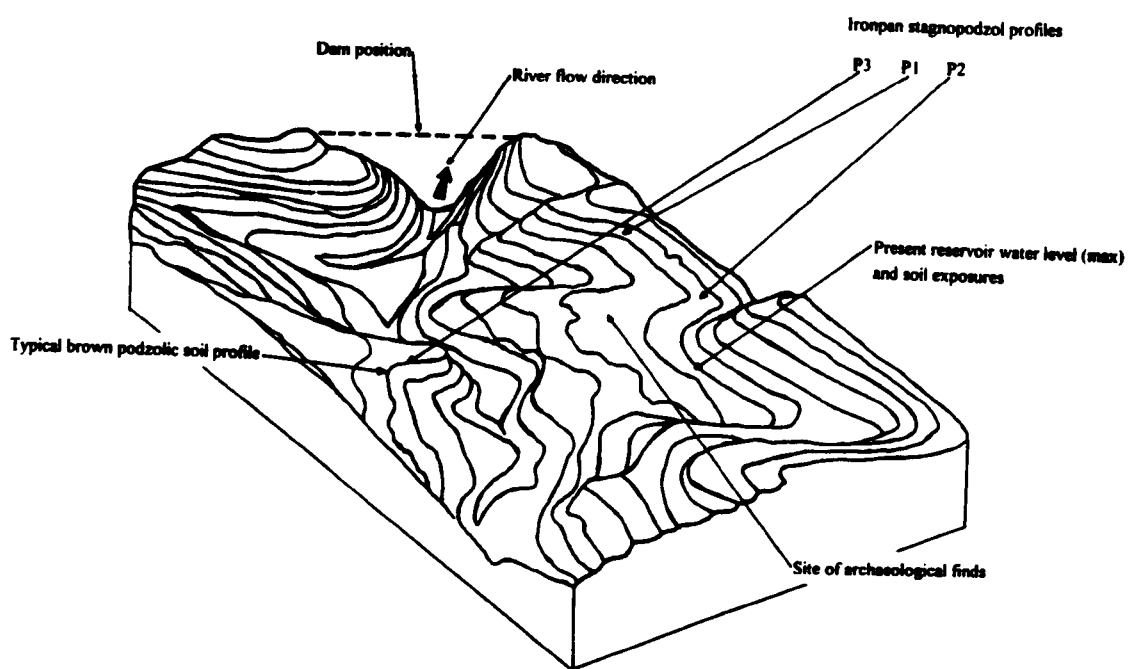


Figure 2.4 A 3-D model of the Aled Isaf Reservoir valley. (Created on GIS SPANS program) showing sampling sites and present water level in the reservoir.

Vale of Clwyd, the annual precipitation being around 760mm. With the increase in altitude across the Hiraethog Moors there is an associated increase in rainfall, with the moors near Llyn Alwen and Llyn Aled receiving up to 1270mm of rainfall a year (a well documented phenomenon, *eg* Rudeforth *et al.*, 1984), composed of both orographic and convectional rainfall (Ratcliffe, 1959). With altitude there is also a decrease in average monthly temperatures and an increase in frost incidence, as well as an increase in the frequency, amount and duration of snowfall and snow cover (Manley, 1971). The number of days on which there is a minimum temperature below freezing point rises from around 30 on the coast to around 50 on the moorland, whilst frosts are more frequent in the east than in the west. Clouds lying low over the hills produce some hill fog in the autumn and winter, but this tends to be restricted to the upland areas. The prevailing winds lie between the south-east and west, northerly winds being considerably less frequent (Fairbairn, 1968). Winds are often strong, particularly on the coast, but the annual average number of days with winds of gale force is usually under 10, much less than the average of about 30 in the west of the Llyn Peninsula (Ball, 1960).

2.6 Soils

In areas affected by glaciation, glacial deposits play a major role in determining the parent material for soils, and this is true of soils of the Hiraethog Moors, which, except for some of the shallowest, are developed on glacial drift material and periglacial deposits (Ball, 1960). In other areas this often complicates the parent material by mixing together many rock types but, in the case of the Hiraethog Moors, it is not thought that the area was inundated by foreign ice during the final phase of glaciation (Livingston, 1991) and so drift material is dominantly of eroded local rock types and so the same as the underlying geology.

Pedogenesis is thought to have begun around 14,000 years ago with the loss of the ice sheets from North Wales. The soils formed on the better drained slopes would probably initially have achieved brown earth status (Avery, 1990), but around 5,000 years ago it is thought that continued leaching and acidification of the soils led to an increase in the growth of peat over the area. This change has been attributed to natural causes (Godwin, 1940) and to anthropogenic activities (Moore, 1973; Bennett *et al.*, 1990).

The controlling factors on Mynydd Hiraethog are relief, climate and vegetation since geology, and therefore parent material, is relatively similar across the area. This affords an ideal opportunity to study how soils are affected by these factors once the influence of varying parent material is removed. Rudeforth *et al.* (1984) give the following diagram (figure 2.5) to show how these factors and their interrelationships influences the soil type. Hodgson (1976) gives the average cumulative maximum potential soil moisture deficit as 61mm for a site near the Alwen Reservoir (SH925554), although Rudeforth *et al.* (1984) suggested that on the whole "soil wetness" was a more common problem than "soil droughtiness".

The Aled Isaf Reservoir provides a valuable study site since around 3.25km of soil profile has been exposed by wave erosion and is easily accessible. Figure 2.6 shows the changes in soil series visible around the reservoir margin. The series studied were the Hiraethog (ironpan

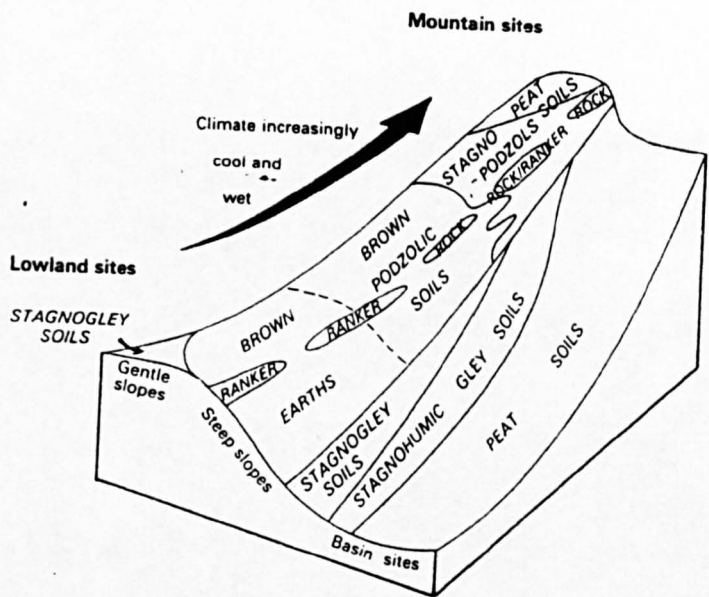


Figure 2.5 Relationships of soils, climate and relief in Wales (Rudeforth *et al.*, 1984).

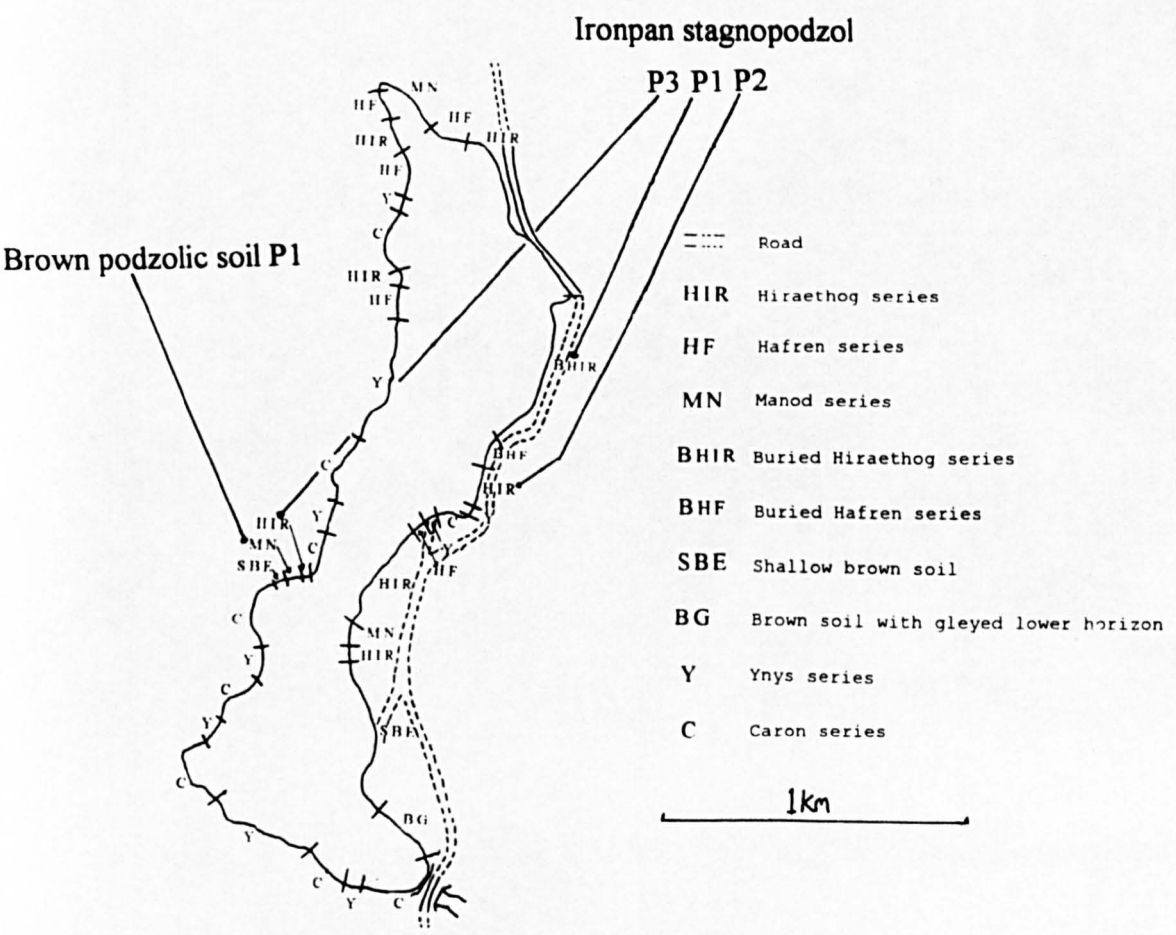
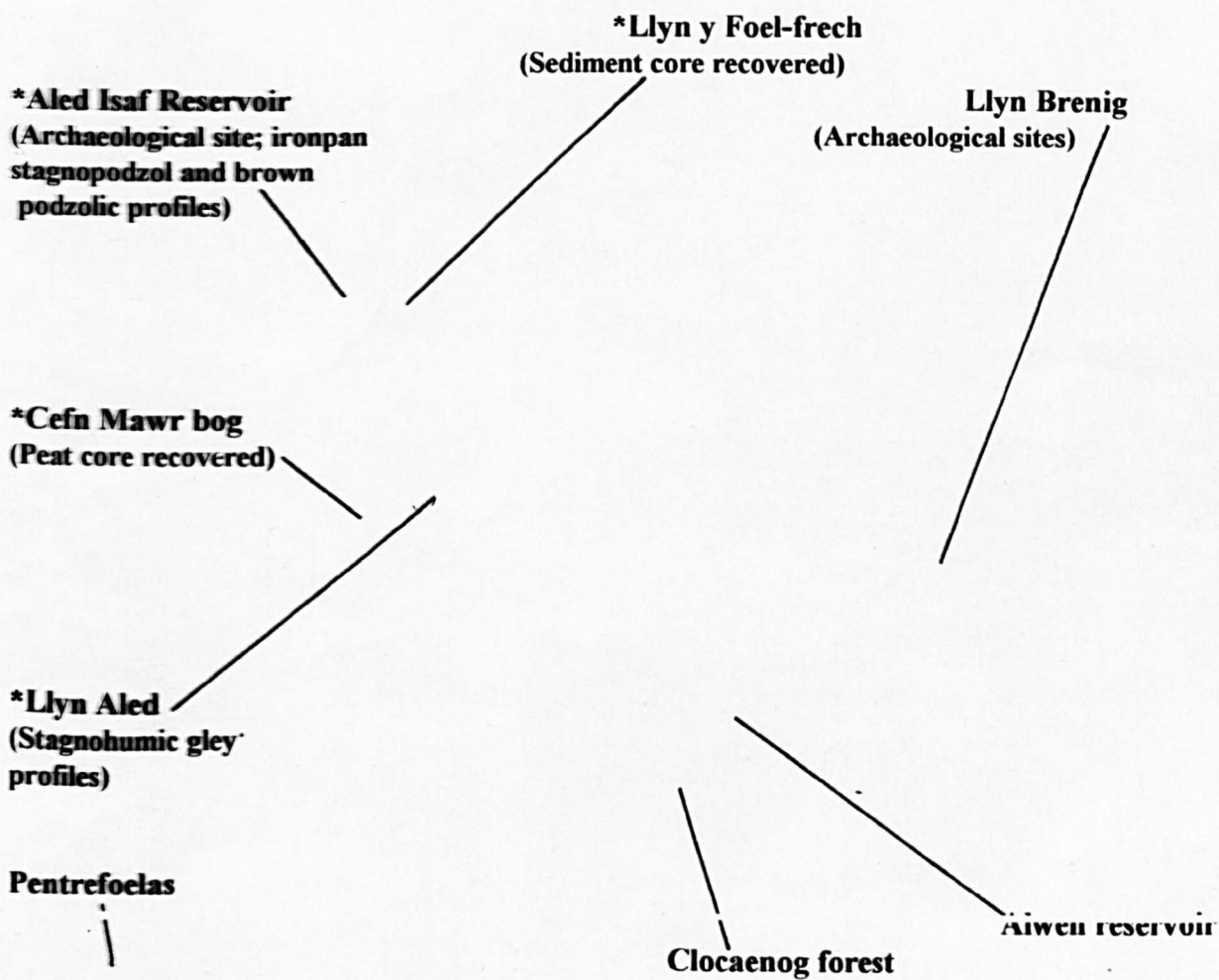


Figure 2.6 Soil profiles exposed around Aled Isaf and the location of some of the profiles studied.

The Hiraethog Moors (sampling sites noted by *).



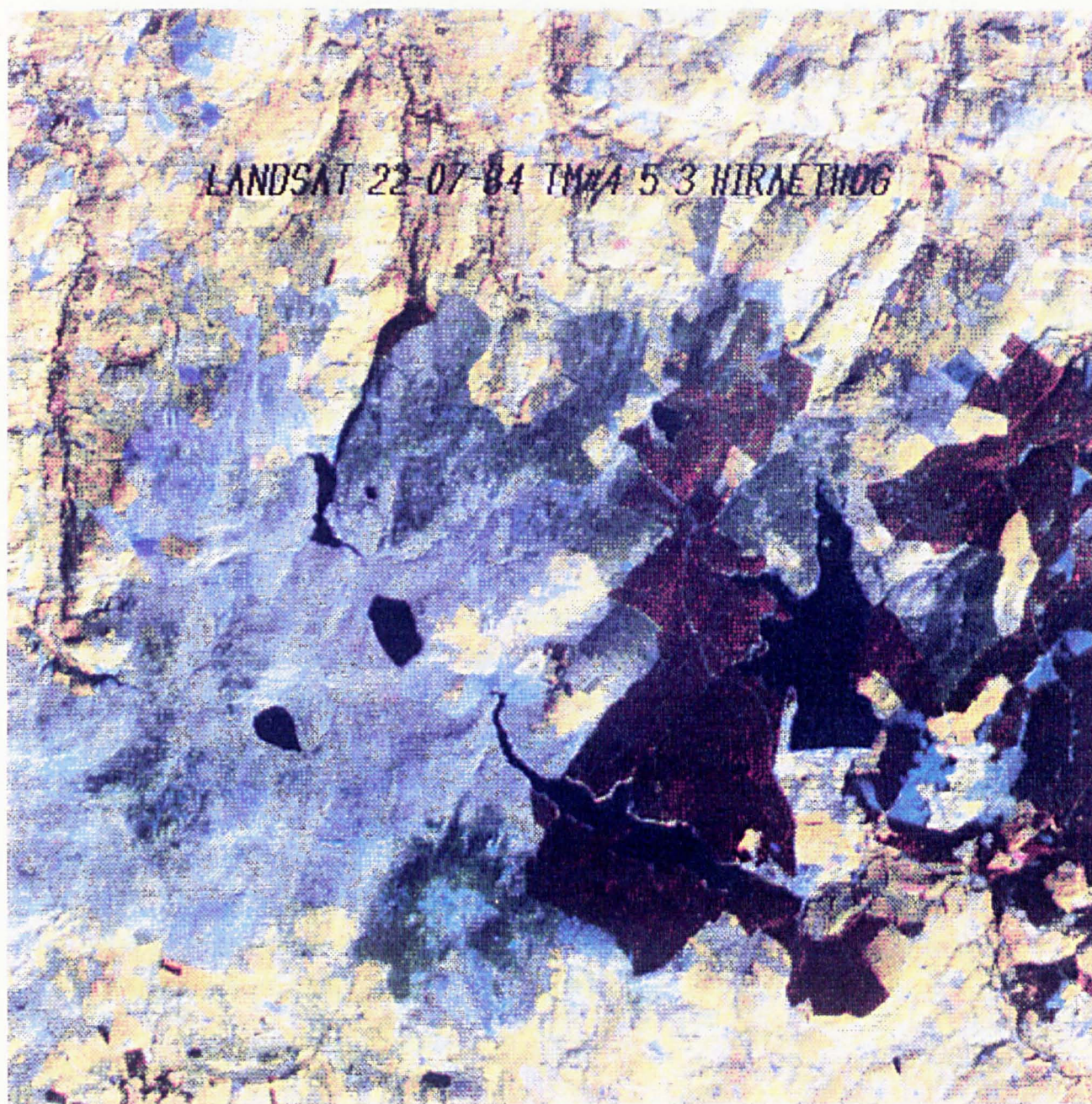


Figure 2.7 Landsat Thematic Mapper image of the Hiraethog Moors (22-07-84; bands 4, 5 and 3).
Blue = moorland
Red/brown = coniferous forest
Black = water
Yellow = farmland

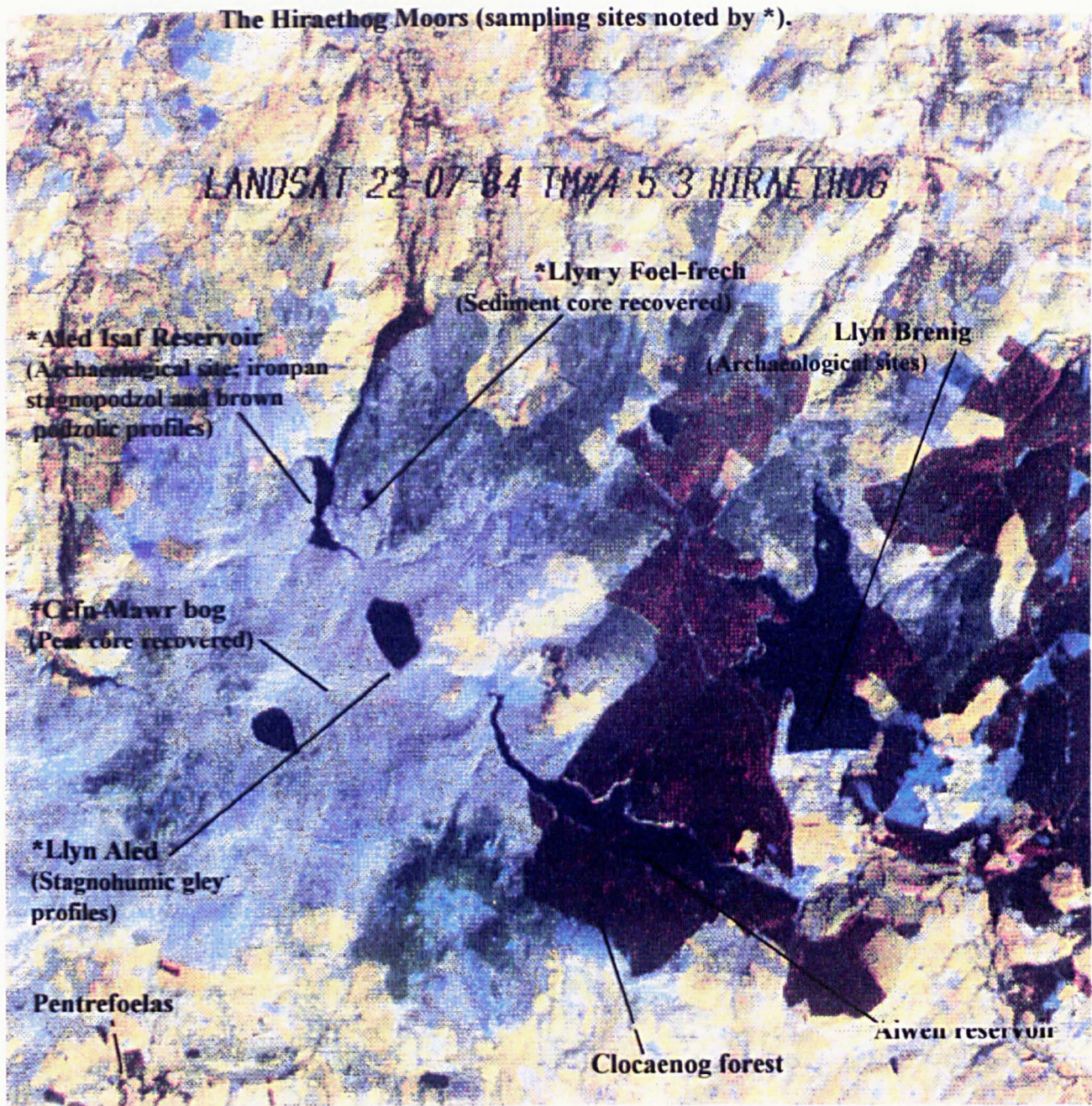


Figure 2.7 Landsat Thematic Mapper image of the Hiraethog Moors (22-07-84; bands 4, 5 and 3).
 Blue = moorland
 Red/brown = coniferous forest
 Black = water
 Yellow = farmland

stagnopodzol), the Freni (formally the Ynys; cambic stagnohumic gley) and the Manod (typical brown podzolic soil). Descriptions of these series can be found in Appendix IV, with their physical and chemical characteristics presented in Appendix II.

Their present day regimes are well documented (*e.g.* Ball, 1960; Bower, 1970; Rezk, 1975; McHugh, 1989; Avery, 1990), as is the origin of the parent material (*e.g.* Livesey, 1966; Lewis, 1970; Bower, 1970; Rezk, 1975).

2.7 Vegetation

Mynydd Hiraethog is an upland area, rising to 520m above sea level. Ratcliffe (1959) suggested that the climatic limit for agricultural cultivation in Wales is around 380m due to extremes of weather and the short growing season. For this reason the upland landscape is dominated by heath vegetation, maintained as such by grazing, typically of *Calluna*, *Vaccinium* and grasses. Bogs are found in the more poorly drained hollows, mainly of *Sphagnum* and *Juncus*. Some of the main boundaries between vegetation types can be seen clearly on the Landsat image in figure 2.7, where the differences between heath, forest, water and improved grazing are visible. Bare rock and scree, whilst being an important part of the Snowdonian mountains, are not so common on the Hiraethog Moors due to the different and uniform geology resulting in gentler slopes. There are also occasional pockets of trees and shrubs scattered over the moorland. Sheep grazing, forestry and water resources are the main land uses of this area. Much of the land is unenclosed, except where improvement techniques have been employed, such as ploughing, liming and fertilising, although continued use of such practices is usually needed to prevent the spread of bracken and heather back over the land (Rudeforth *et al.*, 1984).

2.8 Archaeology

Evidence for human occupation of Clwyd stretches back around 200,000 years (Campbell, 1990), although the earliest evidence for mans presence on Hiraethog itself (from the Brenig and Aled Isaf valleys) has been dated to 8-7,000 BP (Brassil, 1991). The combination of soil exposures and archaeological evidence at Aled Isaf makes it an ideal site for the study of man's influence on the environment and landscape of an upland area during the Holocene. The following is a review of the literature concerning

the archaeological evidence from Clwyd and the Hiraethog Moors, being taken from Manley *et al.* (1991) and Lynch (1993).

Man is known to have been present in North Wales since the Palaeolithic. The earliest site with evidence of human occupation in Clwyd, and indeed in Wales, is Pontnewydd Cave in the limestone escarpment of the Elwy valley. A burnt flint from the same deposit as a human molar was dated by thermoluminescence to 200,000±25,000 BP (end of warm Oxygen Isotope Stage 7c or the succeeding cold stage 7b; Campbell, 1990), and the hominids present at this time are thought to have been of early Neanderthal type. Stone tools and fossilised bones of animals, especially bear, are also found associated with these remains. It has been suggested from the types of artefacts recovered (implements, cores and waste flakes), that both tool manufacture and renewal on site were occurring with a range of other activities taking place. There is also evidence of upper Palaeolithic hunters in other caves in the escarpments of the Elwy and Clwyd, and it has been suggested that this spread was from the north European plain. It is suggested that there is evidence of other hunting bands from southern England at this time, and it is possible that the group that pushed north into Clwyd were following prey such as bear and horse. However, it is also suggested that these groups may have ranged widely across Europe, and occupation of North Wales may have been brief and intermittent, and must have ended altogether with the return of glacial conditions.

Man is thought to have returned to Clwyd during the mid-Devensian. Tools found in the limestone caves of Cae Gwyn and Ffynnon Beuno near Tremeirchion, together with animal bones such as hyena, suggest dates for occupation of around 38 ka BP. With the onset of the Late Devensian glaciation (≈30ka, Livingston, 1990), once again man must have been absent from this area, and it is suggested that the whole of Britain may have been abandoned between 27,000-10,000 BP since tools characteristic of this period have not been found north of the Loire.

The early Holocene (Table 4.1), starting at around 10,000 BP, saw a dramatic change in the landscape as plant and animal species migrated northwards into areas vacated by the ice, spreading from northern Europe across a land bridge. By this time it is thought that pine, birch and hazel woodland had become established, and that woodland animals such as wild ox, red deer and pig would have been the hunter's main quarry. The coastline of Wales is also thought to have differed significantly from that of today, with

the Irish Sea being, in part, an extensive plain although with some channel always separating Britain and Ireland. This land was flooded by rising sea levels over a period of possibly only 200 years, around 8,500 BP, isolating Britain from mainland Europe and Ireland from Wales, leading to a diversification of woodlands to include oak, alder, lime, elm and ash in response to a more oceanic weather pattern.

The Mesolithic is usually placed between 9,950-6,250 BP, and in Clwyd known Mesolithic sites, recognised by the presence of tools made of flint and chert, include Rhuddlan, Prestatyn, Tandderwen, Brenig and Aled Isaf. It is suggested that the finds at Brenig and Aled Isaf originate in the later Mesolithic, around 7,500 BP, and both sites are thought to have been summer hunting camps, with more permanent base camps possibly being located in the zones between the upland and the coastal plains, although during most of this period the coastal plain was much more extensive than it is today.

The evidence available for the reconstruction of human activity during the Neolithic period in Clwyd is again sparse. Only around 15 possible sites have so far been located, although it is suggested that a wide range of terrain was being utilised, with some crops and animals beginning to be domesticated. However, since the species involved were not native to Britain, it is thought that there was some element of colonisation from abroad, although the nature of the transition between late Mesolithic and early Neolithic cultures in this region still seems unclear. From studies of flintwork and stone axes it is suggested that the Mesolithic population of Denbighshire, especially the Clwyd valley, was comparatively large and so its influence persisted further into the Neolithic period than in other areas. It now seems to be generally accepted that, towards the end of the Neolithic, settlements began to move into higher ground, and the discovery of late Neolithic material in moorland valleys, such as at Brenig and Aled Isaf, seems to confirm this, suggesting a wider pattern of land use probably occasioned by a combination of soil exhaustion on lower lands due to long use, a climatic improvement making the uplands a newly exploitable resource, and social pressures from an expanding population. This marks the beginning of Man's positive impact on Hiraethog.

Because of the paucity of Neolithic evidence, it is difficult to know how great the social changes were between the late Neolithic and the Bronze Age. It is suggested that by this time Clwyd had become far more integrated into the cultures of neighbouring

regions to the west and north east, sharing with them traditions of burial and ceremony, and partaking in the same marketing networks. The Bronze Age is, however, marked by the tradition of building circular monuments, as is clearly exemplified at Brenig. Work carried out on pollen from turves beneath Brenig monuments suggests that this period was one of an open landscape suitable for both pastoralists and arable farmers, with cereal crops being grown on land which cannot have been too far from the cemetery in the head of the valley. This evidence for agricultural activity, as compared to hunter-gatherer type communities, is augmented by the possibility that cairnfields, groups of small stone mounds interpreted as the effort to improve the land by stone clearance, may belong to the early Bronze Age, although such features are very difficult to date. However, from the conspicuous positions chosen for many of the barrows across Hiraethog, it is possible that by this time political and/or religious networks had been set up. For example, three barrows on the northern edge of Hiraethog are noted for their striking commanding positions (Mwdwl Eithin, Boncyn Crwn and Gorsedd Bran), and are intervisible so providing a great chain of contact running right across the county. This also implies a fairly open landscape at this time, on the hill-tops at least.

By the late Bronze Age it is thought that communities had moved back down into the central valleys so that, although the fertile valleys of the Elwy and Aled and the headwaters of the Alwen and Clwyd would have been occupied, the central massif of Hiraethog itself would have been unoccupied. This movement and the concentration of population into enclosed settlements is thought to have been a hallmark of the later Bronze Age and Iron Age in many upland regions of Britain. However, apart from the obvious hillforts, of which there are over 30 in Clwyd, other evidence of Iron Age activity is very scarce, much of it possibly having been destroyed by later agricultural activity. However, it is possible that Hiraethog was not totally abandoned, and that some small scale occupation did continue, if only during the summer. There is evidence, from pollen studies, for continued agricultural use of Brenig and of an Iron Age house in the Brenig valley (Brenig 48); a possible Iron Age house has also recently been excavated just north of Cerrigydrudion. Iron Age burial sites are also very rare in Clwyd, especially from the earlier part of the period. The religious manifestations which followed the barrow and circle building era are far from clear, but studies suggest that there is positive evidence of the cult of "offerings" in watery places and in natural groves. The Bronze Age also saw important mining activity for copper on the Great Orme to the north-west for which large quantities of wood are thought to have been required.

By AD 78 it is thought that the two tribes present within Clwyd, the Deceangli and the Ordovices, were almost certainly suppressed by Roman forces. However, no Roman forts are known in Clwyd, although it is suggested that the area benefited from Roman occupation with tile works at Holt, stone quarrying above Wrexham and lead mining from Minera to Halkyn. Stone-built farmhouses survive as striking evidence for this development to the west of Clwyd, but these are absent east of the Conwy, where the natural building material was more likely to have been wood. This emptiness of Clwyd may, therefore, be only apparent although the Romans may have had very little interest in the high moorland which had no known mineral resources and scant agricultural value by then.

The period 400-1,050 AD in Wales is described as the Dark Ages, and it is suggested that the history of the north-east remained even more shadowy than the rest due possibly to Clwyd being between the powerful kingdom of Gwynedd to the west and increasing Anglo-Saxon penetration from the east, preventing the emergence of any strong regional identity and resulting in a lack of archaeological evidence. This is augmented by the fact that areas such as the fertile Vale of Clwyd, where one would expect a comparatively large farming community, are those where the evidence is most likely to have been destroyed by later agricultural activity.

By the 12th century much larger areas of land are thought to have been given over to cultivation by a number of monastic estates throughout Wales, possibly exemplified in Clwyd by Hen Denbych, although this may have been an ecclesiastical estate centre. The dissolution of these monasteries in the 16th century saw a spread in sheep rearing, an example possibly being Hafod Nant y Grafolen (Brenig 48), with the necessary consequence of further woodland clearance and the creation of open field systems such as at Llanynys. Increased pressure from the growing population of N. Wales led to further woodland clearance through the 17th and 18th centuries, with the 1801 Enclosure Act bringing the remaining moorland into private ownership resulting in an increase in the sheep population.

Since then Hiraethog has been managed specifically as a grouse moor, by the burning of heather to promote new shoot growth, and by the grazing of sheep. The North Wales Wildlife Trust now manages a small area near Llyn Brenig (A. Emery, pers.comm., 1994), using flailing, grazing and burning to manage the moorland. Peat cutting has

taken place in some areas, such as around Llyn Alwen (SH8956), and moss is still collected by hand for horticultural purposes from the margins of Llyn y Foel-frech. None of the sites of peat accumulation studied for this project, however, showed signs of disturbance.

Chapter 3. Soils of the Hiraethog Moors

3.1 Introduction

Two soil types, stagnogley soils and stagnopodzols, occur extensively across the Hiraethog Moors and other upland areas of Britain. This chapter aims to review the literature concerning the development of these distinctive profiles in terms of their general physical and chemical properties, clay mineralogy and micromorphology. This will allow the profiles studied to be classified according to the schemes set out by the Soil Survey of England and Wales (SSEW) and the United States Department of Agriculture (USDA). This will then allow a direct comparison of the data collected with published material since these soils, particularly ironpan stagnopodzols and stagnogleys, have been extensively studied in terms of their micro-mineralogy (Livesey, 1966; Rezk, 1975; Chapman, 1986), moisture regimes (McHugh, 1989) and general physical and chemical characteristics (Ball, 1960; Avery, 1990). It is also hoped that a study of these soil characteristics will help answer some of the outstanding questions concerning the development of such profiles in terms of the processes that have operated during the Holocene.

3.2 Soil Classification

Ironpan stagnopodzolic soils, according to Avery's (1980, 1990) classification for the SSEW are a soil sub-group, belonging to the soil group stagnopodzols and the major soil group podzols. Similarly, cambic stagnogleys are a soil sub-group within the soil group stagnogley and the major soil group surface water gley (pseudogley). The typical brown podzolic soil is a sub-group within the soil group brown podzolic soils and the major soil group podzols.

The USDA classification system, although designed mainly for use in the United States, is now used internationally. In this system stagnopodzols would be termed plaquods and stagnogley soils termed cryaquepts, placing them in the spodosol and inceptisol orders respectively. The brown podzolic soil would be classified as an ochrept in the inceptisol order by this system (Avery, 1990)

3.3 Occurrence of stagnopodzols and stagnogleys

These profiles are associated with the cool humid and perhumid uplands of temperate areas characterised by perudic or aquic moisture regimes (Avery, 1990). Ball (1960) suggests that they occur throughout Western Europe, Russia, Eastern Canada and New Zealand, and occupy more than 15,000 km² in England and Wales alone, usually above 250m O.D.. Ball (1960) also states that stagnopodzols and stagnogleys make up 5,120 ha in the region around Rhyl and Denbigh, over 7% of the area, and that this is concentrated in the uplands on the Hiraethog Moors.

3.4 Soil Characteristics

3.4.1 Stagnopodzolic soils

Stagnopodzols and stagnohumic gleys are both characterised by a peaty topsoil but markedly different underlying profile morphologies and characteristics (Ball, 1960). Rudeforth *et al.* (1984) and Avery (1990) suggested that the soils classed as stagnopodzols have as essential features either a thin ironpan (B_f) directly below the eluvial (*ie.* ironpan stagnopodzols) or B_h horizon or a gleyed eluvial horizon (E_{ag} or E_g) overlying a B_s and no immediately underlying gleyed horizon, as well as a peaty surface layer where undisturbed by cultivation. Avery (1990) distinguished stagnopodzols from the other soil groups in the podzolic soil major group by the presence of this peaty surface horizon and the hydromorphic conditions in the surface mineral horizon. Crompton (1952), from studies of ironpan podzols, noted a high level of consistency in the morphology of ironpans, with even the thinnest specimens having an upper half which is black and a lower half which is rusty-brown or kidney coloured, as well as a root mat immediately above the pan which may be continuous or be decomposed to leave only a film of greasy humus on the upper pan surface, the importance of which is not fully understood. Pyatt (1970) sets apart those soils with a thin ironpan as ironpan soils in Forestry Commission surveys.

3.4.2 Stagnogleys

Rudeforth *et al.* (1984) included in stagnohumic gley soils those with an acid organic surface layer and underlying clay loam or sandy clay loam horizons which are grey and strongly mottled, with the mineral layer directly below the peat often being stained with

organic matter. Murphy (1984) stated that some 30% of England and Wales is covered by surface water gley soils (*ie.* stagnogleys) making them the second most widespread major soil group after brown soils. Characteristic features given include those outlined above (for stagnohumic gleys) as well as few or widely spaced macropores and a measured air capacity of normally 5% or less. However, difficulties arise in the classification of these soils at subgroup level (SSEW), particularly in the distinction between typical (argillic) and cambic subgroups. Murphy (1984) suggested several reasons for an increase in sub-soil clay content: clay translocation; inherited heterogeneity within the parent material or the production of clay through *in situ* breakdown of coarser particles.

A more general problem associated with the soils of the Hiraethog Moors is the type and uniformity of the parent material. Whilst removing one of the variables in soil development and so allowing the effect of other factors to be determined, the fact that the parent material has a high silt and clay content means that disaggregation has the potential to result in a heavy textured soil prone to gleying and therefore, in any situation leading to a collapse or loss of structure, gleying is likely to be the result.

3.4.3 Brown podzolic soils

Avery (1990) stated that the typical-subgroup of brown podzolic soils is by far the most extensive and is characterised by having a B_s horizon which passes downwards into an unmottled BC or C, or rests directly on bedrock. He suggested that they usually have a loamy texture. The B_s usually lies below an A_h, or A_p where cultivated, with no intervening E or B_h horizon of significant thickness. Avery (1990) proposed that they are widely distributed at altitudes up to 400m in humid and perhumid areas of the British Isles but are only very sporadically represented in the subhumid lowlands, and that these soils in Upland Wales, the Lake District and the Southern Uplands of Scotland originally bore oak forest with acidophile ground vegetation, although they now support acidic grassland with bracken or coniferous plantations.

Intergrades to stagnopodzols are common on upper slopes in perhumid upland localities and include profile forms described as "podzols with gleying" (Avery, 1990). This is a spatial sequence, but is also suspected to be a temporal sequence, representing the changes which have occurred in some soils over the Holocene and forms a central theme to this research project.

3.5 Environmental aspects of soil development on the Hiraethog Moors

The development of all such profiles is favoured by increasing altitude, northerly aspect, humidity and coolness. They are associated primarily with mor humus- (L/F/H) and peat- (Oh) forming ericaceous vegetation and semi-natural grassland (*Molinia*, *Deschampsia*, *Nardus* spp. with *Eriophorum*, *Tricophorum*, *Sphagnum* and *Juncus* spp.) occurring in wide association with blanket peats (Avery, 1990). As shown in Fig. 2.5 (Rudeforth *et al.*, 1984), the stagnopodzols occur as upper-slope members of toposequences with podzolic brown soils on lower slopes and bog soils and staghohumic gley soils on flatter ground, especially where the substrata are impervious and in sites receiving water from higher ground.

Upon the retreat of the last glaciers from North Wales some 14,000 years ago (Coope and Brophy, 1972) soils of the Hiraethog Moors began to develop and have since evolved to their present day status in response to changing climate, vegetation and the influence of man. After woodlands reached their climax some 5-7,000 years ago (Watkins, 1991), forest clearance began, due to a deteriorating climate and/or to increasing human impact on the environment.

Removal of vegetation interrupts the bio-geochemical cycling of an ecosystem, while vegetation change can induce fundamental alterations in the physical and chemical status of soils (Miles, 1985). In the cool humid British uplands, such changes are thought to be associated with the expansion of ericaceous and grass heaths (*Molinia/Nardus/Deschampsia*), the accumulation of organic matter, gley and/or podzolic processes and the widespread occurrence of blanket peat, staghohumic gley soils and stagnopodzols (Maltby and Caseldine, 1982). The changes in vegetation during the Holocene are discussed further in chapter 4, as well as the possible impact of man on the landscape. The rest of this section will concentrate on the processes thought to be involved in the formation of stagnopodzols and staghohumic gley soils.

3.6 Soil development - a review

3.6.1 Soil chemical and physical properties

3.6.1.1 Gley soils

The chemical and mineralogical transformations involved in soil reduction and the mechanisms responsible for gley morphology are well documented (Bloomfield, 1951; Siuta, 1967; Brewer and Sleeman, 1970b; Thomasson and Bullock, 1975; Campbell and Schwertmann, 1984). Siuta (1967) suggested that the direct cause of the development of gleying was a negative oxygen balance of the soil environment, and that water was not the direct cause of gleying, rather having a role in this process by limiting the exchange of air between the soil and the atmosphere and by the creation of a suitable environment for the growth of micro-organisms and for chemical reactions between the organic and mineral components of the soil. Reduction of soil constituents under the influence of organic matter alone has been shown to be thermodynamically possible (Bloomfield, 1951), although reaction rates are very slow. It is therefore generally accepted that significant soil reduction occurs only when organic matter and temperature allow microbial activity to occur so that, in the absence of oxygen, soil constituents act as terminal electron acceptors in the respiration of soil organisms which derive their energy from the decomposition of thermodynamically unstable products of photosynthesis (Ottow, 1973).

Pyatt *et al.*, (1979) and Pyatt and Smith (1983), working in Newcastleton Forest in the Scottish Borders, found that the water table fluctuated between 0-15cm of the peat upper surface and therefore usually lay within the peat from autumn to spring with water potentials being close to zero in the subsoil for much of the year. In summer, the water table fell to 70cm and, whilst some drying occurred, potentials fell to only -100cm H₂O in the upper horizons, from which it could be inferred that much of the soil was constantly wet.

Thomasson and Bullock (1975) suggested that the main genetic process in surface water gley soils is a reduction and segregation or removal of iron as a result of saturation by a water table held above an impervious layer, and a slowly permeable horizon is thought to be the main characteristic determining their morphology (Murphy, 1984). In the cool humid uplands, the prevailing conditions of surface wetness and

acidity are also thought to cause intense reduction and mobilisation of iron in the upper part of the mineral soil, even where subsurface horizons are relatively permeable (Avery, 1990). Stagnohumic gleys on clayey materials typically possess a clayey prismatic B_g with prominent vertical fissures and a structureless or platy C which is noticeably less wet. Thomasson and Bullock (1975) also suggested that in cases where there is a slow reprecipitation of iron (Denchworth soil - pelostagnogley) its redistribution throughout the soil material is favoured which may result in a complete loss of iron in the drainage water or, in soils with restricted drainage, in a coarse pattern of mottling.

Thomasson and Bullock (1975) examined mottle composition, micromorphology and hydrology of some lowland stagnogleys. Using selective dissolution techniques they found that profile maxima of dithionite extractable free iron oxides coincided with the most mottled horizon, most of the iron occurring within the mottles themselves. From extractions with oxalate and pyrophosphate they suggested that the iron was not generally present as amorphous hydrous oxides or associated with organic matter but occurred as a more crystalline form. Campbell and Schwertmann (1984), in studies of lowland stagnogleys, suggested that the low ratio of oxalate to dithionite extractable iron indicated rapid ageing and a high degree of crystallinity consistent with the presence of goethite and lepidocrocite, indicative of hydromorphic processes in mottled horizons. Pyrophosphate extractable forms of carbon and aluminium showed no such differentiation, therefore organic mechanisms of mobilisation were not involved. Similar trends in stagnohumic gley soils possessing an acid peaty topsoil have yet to be demonstrated.

Brinkman (1970) suggested that a process termed ferrolysis was a major genetic process in many pseudogley soils of Europe. It is suggested that this process involves cation exchange reactions, involving iron, in an orderly sequence of reduction-oxidation cycles, leaching of displaced cations in the reduced phase and acid attack of clay minerals in the beginning of the oxidised phase of each cycle, the pH in the oxidised phase becoming lower as exchangeable bases are eliminated and replaced by mainly aluminium from the lattice after oxidation. Brinkman (1970) suggested that this would account for, among other things, the presence of Al-interlayered clays and the apparently greater speed of podzolisation in seasonally wet conditions.

3.6.1.2 Podzolic soils

Podzolisation processes have been reported to be effective over very brief periods. Crompton (1952) noted the formation of ironpan podzols in fields ploughed within the last hundred years, whilst other workers (Bloomfield, 1955) have noted the formation of podzols under coniferous woodland (Norway spruce and Kauri pine) in the last 85 years. Muir (1934), working in the Tiendland Forest in Scotland suggested two mechanisms for podzol development. The first was the development of anaerobic conditions below the dense ericaceous root-mat of a non-podzolic soil, leading to reduction, mobilisation and subsequent reoxidation of iron in the aerobic subsoil as an iron pan. The second was the formation of an ironpan in podzols *sensu stricto* leading to impeded water movement, superficial anaerobism and the development of a peaty surface horizon.

Crompton (1956) supported the first theory due to the observed often discontinuous nature of the iron pan which presents little impediment to water movement. He proposed that iron reduction and mobilisation occurred under the influence of peat and saturation, along with possibly more complex processes involving podzolic mechanisms (Bloomfield, 1955), and was followed by reoxidation in the aerated subsoil. Such mechanisms would allow the pan to redevelop further down the profile and would account for the convoluted nature of many iron pans (Crompton, 1952). Pyatt *et al.* (1969) described transitions from brown earths to ironpan stagnopodzols in Wales which supported Cromptons (1956) proposals. Pyatt (1970) also considered Muirs first theory of superficial anaerobism in podzols to be the most widely applicable in upland podzols.

Avery (1990), in a review of studies of water and aeration in German and Scottish stagnopodzolic profiles suggested that there was evidence for anaerobism in the horizons above the ironpan for at least part of the year, with horizons below remaining aerated. He suggested that this waterlogging of the surface horizons was due more to adverse pore size distribution, and therefore low hydraulic conductivity, than to the ironpan which was seldom entirely continuous. This conclusion supported the hypothesis, previously advanced by Muir (1934), Crompton (1956) and Crampton (1963), that the characteristics of the upper mineral horizons have been superimposed on those of pre-existing well aerated soils as a result of superficial peat formation, which was thought to have been promoted over much of upland Britain by the decline

or clearance of forests (see Chapter 4). The occurrence of ferric stagnopodzols, profiles which have similar organic and eluvial horizons but which lack an ironpan, in the same slope facet is proposed to further support this theory (Avery, 1990).

The characteristic B_h horizon overlying ironpans of podzolic derivation (iron-humus stagnopodzol of Avery, 1980) is often absent in England and Wales (Crampton, 1963). McKeague *et al.* (1967) suggested that the precipitation of fulvic acid-Fe/Al complexes is a possible mechanism for the formation of initially organic-rich ironpans, with organic matter subsequently being consumed by micro-organisms to give rise to organic-impooverished pans. However, they suggested that this is unlikely to be the full picture since it does not account for the thinness of pans, the high Fe/Al ratios compared to other horizons and the high Fe/Al molar values compared to the organic matter. McKeague *et al.* (1983) concluded that the mechanisms leading to the formation of a thin ironpan have yet to be elucidated, although many workers favour redox mechanisms for pan development (Righi *et al.*, 1982; McKeague *et al.*, 1983; Pyatt and Smith, 1983).

It is not clear what role amorphous materials, such as allophane, imogolite and proto-imogolite, play in the formation of these soils. Allophane in podzol B horizons was first reported by Franzmeier *et al.* (1963), in Michigan podzols, but its role in the podzolisation process has only recently received sustained attention. Once considered a by-product of the transport of material in podzols some researchers have now attributed allophane a crucial role in the podzolisation process itself (Farmer *et al.*, 1980; Farmer, 1982; Anderson *et al.*, 1982).

Anderson *et al.* (1982), working in Scotland, examined the morphology and chemistry of ironpan stagnopodzols and considered them to be the final stage in an evolutionary sequence *ie.* iron podzol \Rightarrow iron humus podzol \Rightarrow ironpan stagnopodzol. They proposed that Al and Fe are initially brought into solution by non-complexing inorganic acids and readily biodegradable small organic acids. Fe and Al, subsequently transported as positively charged inorganic sols, are deposited as oxyhydroxides (Fe) and amorphous allophanic or imogolite type materials (Al + Si) in the B_s horizon of an iron podzol. With increasing wetness during rainfall periods they suggested that colloidal and soluble organic matter descends through the unreactive E_a until it encounters and is adsorbed by the Fe and Al at the top of the B_s which then acts as a trap for any Fe and Al subsequently remobilised. They proposed that this is the humic

acid rich B_h of the humus iron podzol, fulvic acids penetrating the B to greater depth.

Under wetter conditions, due possibly to the influence of a thickening peaty surface horizon, they suggested that percolation is impeded by the amorphous and often cemented B_f, ferric humate of the B_h is reduced, Al replacing Fe which is deposited at the interface between seasonally reducing conditions above and permanently oxidising conditions below. Anderson *et al.* (1982) concluded that this mechanism of ironpan formation explained their locally discontinuous nature and erratic pathway through profiles, since the boundary of a perched water table which initiates the pan formation is critically dependent on slight textural changes.

Buurman and Reeuwijk (1984) proposed a model for the development of podzol morphology and the formation of allophane in the illuvial horizon of podzols, suggesting that there is evidence to support the role of complexing organic compounds in this process, but not evidence to support a role of short range order aluminosilicates such as proto-imogolite, as proposed by Anderson *et al.* (1992). Buurman and Reeuwijk (1984) suggested that, contrary to that proposed by Farmer *et al.* (1980) and Anderson *et al.* (1982), supply and turnover of organic compounds would be sufficient to allow appreciable amounts of Fe and Al to accumulate due to transport by such complexing agents whilst organic matter levels remain low, supporting the idea, proposed by McKeague *et al.* (1967), that organic matter is subsequently destroyed by microbial activity.

Buurman and Reeuwijk (1984) report that allophane is not known to exist in podzol eluvial horizons and suggested that this was due to its removal by organic complexing agents from this horizon. They proposed that, in some Scottish podzolic profiles studied, all aluminium is organically bound and that the movement of iron in the absence of organic matter is too slow to produce any recognisable iron containing B horizon within some hundred thousand years. They concluded that mobilisation, translocation and precipitation of "sesquioxides" by complexing organic compounds was the most feasible explanation for the presence of allophane in podzolic profiles.

However, Farmer (1984) disagreed with such a model, suggesting that it failed to predict the observed distribution of allophane. He proposed that the most economical and flexible theory to account for podzolisation processes and the diverse range of podzol types required a contribution from two differing migrating species. The first is a

"positively-charged mixed $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ sol incorporating minor amounts of organic matter and silicate clay". The second is "negatively charged organic sols and solutions carrying minor amounts of Al, Fe and clay". He suggested that these species can be generated in B horizons, especially where root activity is high, and that they need not be widely separated in time. Farmer (1984) accepted the proposal by Buurman and Reeuwijk (1984) that small organic molecules have a role to play in the dissolution of minerals and of previously deposited Fe and Al hydroxides but concluded that they will be rapidly metabolised and so not reach the zone of imogolite formation. Farmer (1984) suggested finally that the "presence of aluminium and iron humate and fulvate complexes in podzol B horizons can always be explained by reaction *in situ*, rather than by illuviation. In contrast, the site of occurrence and micromorphology of allophane, and the presence of imogolite, requires a proto-imogolite mobile phase".

Micromorphological and analytical studies carried out by Farmer *et al.* (1985) and Milnes and Farmer (1987) on allophane coatings in the upper Bs produced atomic ratios for pure allophane of Si:Al:Fe = 1:2.48(± 0.16):0.29(± 0.08), with darker areas showing a small increase in iron content. Farmer *et al.* (1985) suggested that this small difference in Fe could not account for the observed colour difference, suggesting some incorporation of organic matter. From such evidence they suggested that the origin of allophane is related to intense weathering of plagioclases and biotites in surface horizons, and that the material is deposited from solution and not formed *in situ* from precipitated organic complexes.

Milnes and Farmer (1987) proposed that there is no good evidence for the transformation of allophane to kaolinite in the upper B horizon, as suspected by Farmer *et al.* (1984a). They suggested that their observations do support the view of Anderson *et al.* (1982) and Farmer (1982) that the influx and precipitation of organic matter in podzol B horizons has little to do with the deposition of allophane, citing evidence that organic matter possibly has an important role in preventing the formation of allophane through the development of humus-Al complexes. They concluded that the system is, however, a dynamic one in which fluctuating conditions can favour renewed formation and deposition of allophanic material such that organic-rich deposits in dissolution zones can become encapsulated by later deposits of allophane matrix.

Subsequent work by Lundström and Öhman (1990) has shown the effects of organic acids in enhancing weathering and the dissolution rate of cations, an effect that was

seen to drop off when samples were inoculated with microbes, suggesting microbial degradation of the complex-forming organics, a process thought to be of significance in the formation of the illuvial horizon. Lundström (1993) also showed that, in Swedish podzols he studied, 80% of the monomeric Al in the upper soil was bound in organic complexes, and that the concentration of organic acids and organically bound Al declined sharply with depth.

3.6.1.3 Summary

From this discussion it becomes obvious that there are still conflicting views and many questions yet to be answered concerning the chemical processes which have led to the formation of these characteristic soils. The debate seems, at present, to be concentrated around the relative importance of allophane materials as compared to organic compounds in the eluviation, translocation and illuviation processes occurring in such soils. However, it is unlikely that an answer to this problem will be forthcoming from chemical data alone, and clay mineralogical and micromorphological evidence is needed to back up proposed models. Both techniques are used in this study, and the following two sections aim to review the literature on these topics in relation to the soils found over Hiraethog.

3.6.2 Clay Mineralogy

Clay mineralogy, *ie.* the mineralogy of that fraction $<2\mu\text{m}$ equivalent spherical diameter, is an important characteristic of a soil in that it provides information on parentage and on pedogenic processes that have occurred over time (Moore and Reynolds, 1989). Work carried out by Rezk (1975) and Chapman (1986) showed that the soils of Hiraethog, derived from Silurian siltstones and mudstones, contained quartz, hydrous mica, chlorite and vermiculite, with about half as much chlorite as mica (Loveland, 1984), and that inferences could be drawn from the distribution of these and other clay minerals down the profiles concerning both present and past pedogenic activity.

3.6.2.1 Formation of clay minerals found in Hiraethog soils

The mineral fraction of soils is produced by the transformation of parent materials which are subject to a twofold process: (i) physical and mechanical desegregation

without chemical modification of the minerals; (ii) chemical weathering causing a transformation of primary minerals with the formation of secondary minerals, particularly clay minerals, which make up the weathering complex (Duchaufour, 1982). Shahid (1988) reviewed the processes thought to result in the presence of clay minerals in soils, suggesting that this was closely related to the weathering environment and the various weathering processes that the parent materials were subjected to. These could be divided into three categories: (i) inheritance (ii) transformation (iii) synthesis.

Inheritance of clay minerals from the parent material can occur without mineralogical change, and in the case of the Hiraethog Moors, where the parent materials are silt- and mudstones rich in micas and chlorite, these will be transferred directly to the clay fraction of the soil. Chapman (1986) suggested that in cases where chemical modification was limited, many clay minerals persist metastably, and that in such situations the clay mineralogy of the soil would be determined by the parent material. However, clay minerals are likely to be transformed, with time, into other clay minerals by weathering, and as such in most soil types the clay mineralogy differs considerably from that of the parent material except perhaps in the lowest, and least altered, horizons. This results in progressive alteration of components from the lowest to the uppermost horizon.

The processes responsible for such transformations have been described as "degradation" and "aggradation" by Duchaufour (1982). Degradation relates to the loss of substances from clay minerals (K^+ , Mg^{2+} , Fe^{2+}) with the introduction of water, and hence mica and chlorite minerals are changed to expanding minerals through this process *via* a series of mixed-layer intermediates (Jackson, 1964). During aggradation, construction and gain of constituents into crystal lattice structures takes place in which case the transformations will be in the opposite direction to degradation. This process is very rare in weathering environments, but may be operative in zones of accumulation and in some hydromorphic soils (Shahid, 1988). The third process, synthesis, involves the formation of minerals from the dissolved and amorphous products of weathering. Barshad and Kishk (1969) suggested that dioctahedral vermiculite may be formed by synthesis. Rai and Kittrick (1989) give examples of the conditions required for the formation of minerals such as montmorillonite, kaolinite and gibbsite and suggested that these conditions can occur naturally in soils.

3.6.2.2 Stability of clay minerals with particular reference to chlorite

As mentioned above, clay minerals, once physically released from the parent material, may undergo chemical transformations depending on the prevailing environmental conditions, so altering the proportions of minerals to that found in the parent materials. Rezk (1975) and Chapman (1986) showed that soils formed on Silurian silt- and mudstones on the Hiraethog Moors were dominated by hydrous mica, chlorite and vermiculite, and that the proportions of these minerals, especially chlorite, altered between horizons, and there are many other examples in the literature of changing proportions of clay minerals, particularly chlorite, both up and down profiles.

Instances where chlorite increases towards the surface of a profile are thought to indicate the relative stability of chlorite (Glenn *et al.*, 1960; Maclean and Brydon, 1963; Klages, 1969). One of the most spectacular examples of the stability of chlorite in soil profiles is that described by Mitchell (1955). He studied the clay mineralogy of over 50 Scottish soils of various drainage classes and developed on a range of parent materials. He suggested that chlorite only occurred in the clay fraction of soils on chlorite-rich Silurian Shales, and he considered this chlorite to be highly stable since the proportion of the chlorite in the clay fraction increased towards the surface of the profile and was equally distributed throughout the different size fractions within the clay fraction.

Several alternative theories have been proposed to account for this persistence of chlorite. Martin (1954) suggested that some chlorite may have been formed in the A horizon at the expense of minerals by the incorporation of Mg^{++} released by the weathering of mica. Mahaney (1991) proposed a similar weathering sequence, of chlorite formation from illite, in studies of a series of historically dated moraines in the French Alps. Alternatively Tamura *et al.* (1959) interpreted the presence of chlorite in the clay fraction of some podzolic soil surface horizons as an indication of the youthfulness of these profiles and similarly Maclean and Brydon (1963) ascribed the presence of chlorite in A horizons of some Canadian soils to a low intensity of weathering in these soils.

Quigley and Martin (1963) suggested that the increase in chlorite content towards the surface of soil profiles developed on glacial till in New England was due to the high intensity of weathering at the surface which resulted in the oxidation of ferrous to ferric iron within the chlorite structures, giving rise to a better crystallised chlorite with a

lower charge density than that in lower horizons. Ghabru *et al.* (1990) showed a similar relative stability of iron-rich chlorites.

However, the presence of chlorite in the upper horizons of podzols has been shown to relate only to an apparent stability of this mineral in some soils. Beaver *et al.* (1955) considered that the persistence of chlorite in the A_e horizons of some podzols was due to the differential eluviation from these horizons since they found that chlorite was concentrated in the coarse clay and silt fractions. A similar fact was noted by Bain and Duthie (1984) in studies of Scottish podzols. They found that chlorite was dominant in the clay fractions and showed little variation in amount with depth. However, when investigated further they found that the fine silt fraction contained more chlorite than the coarse silt fraction and that in both the amount of chlorite decreased towards the surface. They suggested that chlorite was being dissolved out from the clay fraction, but as chlorite was being broken down and transferred to finer particle size fractions, this dissolution effect was being masked by the replacement of the clay fraction chlorite from the fine silt fraction.

Reported instances which show a decrease in chlorite content both with decreasing particle size and towards the surface of soil profiles is usually taken as an indication of its degradation (Rezk, 1975; Chapman, 1986). Fanning and Jackson (1965) suggested that the absence of chlorite in the upper horizons of a grey-brown podzolic soil, developed on shale derived till parent material in Southern Wisconsin, was due to the instability of chlorite under the prevailing conditions. Similar decreases in chlorite content towards the soil surface have been noted in soils of different drainage classes and widely varying parent materials (Glenn, 1960; Lynn and Whittig, 1966; Post and Janke, 1974; Alias-Perez and Ortiz-Gonzalez, 1984; Righi *et al.*, 1986; Righi and Meunier, 1991). Loveland (1984), in a review of clay mineralogy of soils of North Wales, suggested that there is little evidence for a corresponding decrease in mica content towards the surface of such profiles, and concluded that there had not been significant alteration of illite in soils developed in postglacial deposits.

Studies (Adams *et al.*, 1971; Post and Janke, 1974; Bain, 1977) have been carried out on the weathering of chlorite and illite, and where both illite and chlorite are present the conclusion has always been that chlorite is more susceptible to weathering. Since these studies have involved comparisons of trioctahedral chlorite and dioctahedral illite, this has suggested that trioctahedral phyllosilicates are more readily broken down. This was

confirmed by a study carried out by Roaldset (1972) who showed illite to be the more rapidly broken down when in a trioctahedral form. Rezk (1975) and Chapman (1986) showed that soils of the Hiraethog Moors were dominated by trioctahedral chlorite, and it would be expected that chlorite in these soils will be lost more rapidly than the hydrous mica.

Aurousseau (1988) suggested that clay degradation under acid and humid conditions of siltstones of western Europe may be a primary process, *ie.* that in natural conditions soil cover is acid enough and generates a low enough oxydo-reduction (redox) potential to allow such clay degradation. He suggested that when the primary minerals are micas the clay degradation produces hydroxy-aluminous vermiculites whilst at the same time there are losses of iron, magnesium and potassium.

3.6.2.3 Products of the weathering of clay minerals

There is evidence in the literature that indicates the weathering of clay minerals, such as chlorite, to amorphous alumino-silicate occurs under humid acid conditions such as prevail in many upland areas of Britain today (Kodama and Brydon, 1968; Coen and Arnold, 1972). Where large quantities are present in the soil they are thought to have some influence over soil properties (Kodama and Brydon, 1968), especially since in many instances they are associated with the surface of clays and humus colloids (Carstea *et al.*, 1970; McKeague *et al.*, 1971; Johnson and Yeh, 1974; Wada, 1989). The amorphous materials which are of importance in soils are oxides and hydroxides of Al, Fe and Si, and silicates of Al and Fe, all in various combinations with water (Wada, 1989). The two main types of amorphous materials present in soils are termed allophane and imogolite (Wada, 1989). However, allophane is usually associated with volcanic soils (Wada and Harward, 1974), although allophane-like minerals, such as non-crystalline Al and Fe hydroxides, can occur as major constituents of the clay fraction (Wada, 1989).

The formation of amorphous alumino-silicates is thought to be of importance to the understanding of podzols and podzolisation. The weathering of chlorite to amorphous materials in surface horizons is reported to be a fairly common phenomenon in acid soils. Brydon *et al.* (1968), in a study of a wide range of Canadian podzols, reported that the C horizons were dominated by trioctahedral chlorite and dioctahedral illite which became progressively more altered towards the surface with no indication of the

trioctahedral alteration products in the A_e horizon. From this, and from the completeness of the decomposition of trioctahedral chlorite in HCl (Ross, 1967), they concluded that the chlorite had decomposed and that the weathering of chlorite in podzol A_e horizons was more likely to yield amorphous alumino-silicate.

In a study of pedogenesis on soils derived from Silurian mudstones in Mid-Wales, Adams *et al.* (1971) found that chlorite progressively decreased in amount towards the surface until it was absent in the A_{eg} horizon of a peaty podzol. They suggested that amorphous silica may be the weathering product of the chlorite, but also proposed that the small amount of vermiculite found in some horizons may also be a weathering product of chlorite, a suggestion also made by Adams and Kassim (1983), Caillier *et al.* (1984), Loveland (1984) and Righi and Meunier (1991).

However, in the case of the soils of the Hiraethog Moors this weathering sequence is doubtful. Vermiculite, if derived from chlorite, would be expected to have a trioctahedral structure with Fe- and Mg-rich hydroxy interlayers, whilst if derived from illite it would be expected to have a dioctahedral structure with aluminous hydroxy interlayers. Rezk (1975) showed the vermiculite to be dioctahedral in the E_{ag} horizon of these soils strongly suggesting a hydrous mica origin. Douglas (1989) suggested that the weathering of mica to vermiculite depended on a strong leaching environment to remove solution potassium so the reaction can proceed. Consequently, the intensity of the reaction would be greatest in the A horizon and decrease with depth.

Righi *et al.* (1986), from XRD analysis of podzolic soil clays, suggested that chlorite can weather to intergrade 2/1 minerals, whilst several workers have suggested that chlorite weathers to hydroxy-interlayered intergrade minerals, particularly hydroxy-interlayered vermiculite (HIV) (Harris and Hollien, 1988; Ghabru *et al.*, 1990; Arocena and Pawluk, 1991; Righi *et al.*, 1993). Ghabru *et al.* (1990) found a chlorite-like mineral containing Fe³⁺, whilst most chlorites contain Fe²⁺. When this iron was extracted by dithionite-citrate the mineral collapsed to 1.0nm on K⁺ saturation and on heating, a feature that other iron-rich chlorites do not exhibit. From this they suggested the mineral was an Fe-HIV rather than a true chlorite. They suggested its origin may be due to Fe lost from the octahedral layer of an original mica being responsible for the formation of an Fe-hydroxy interlayer, thereby giving rise to a chlorite-like mineral, or that the interphase resulted from the weathering of an original chlorite since chlorite was detected in the parent material.

Loveland (1984) proposed that sorption of Al into the interlayer space of chlorite can occur when the pH is in the range 4-5.5, and invoked this mechanism to explain the presence of 'chloritized' vermiculite in the upper part of a number of soil profiles. Righi *et al.* (1993) suggested that the next stage is the progressive removal of the hydroxide interlayered sheet and dissolution of the chloritic layers, a much slower process which may yield amorphous material high in silica.

Wang and Kodama (1986) suggested conditions which they considered to result in the formation of imogolite as: (i) low organic matter content in the sola (ii) high ratio of $(Al_o-Al_p)/Al_p$ in B horizons (iii) strong but not extremely acid soil reaction in B horizons (iv) porous nature of the soil. Their findings were consistent with the hypothesis that the downward movement and precipitation of inorganic amorphous forms of Al and Si is a major process in podzolisation. This hypothesis also suggested that the occurrence of imogolite was not restricted to spodosols or podzolic soils.

3.6.2.4 Effects on soil properties of amorphous materials including iron and aluminium hydrous oxides

Brydon *et al.* (1968) considered that the presence of iron and aluminium hydroxide coatings in the B_s protected chlorite against complete decomposition, even over relatively long periods of time, by impeding the uptake of H^+ and the release of Mg^{2+} and Fe^{2+} . The absence of such coatings in the A_e , they concluded, would therefore allow complete decomposition of chlorite in this horizon. A similar situation was reported by Wang *et al.* (1989) who again suggested that the resistance of crystalline Fe oxide coatings to weathering and decomposition could protect soil clays from weathering. In more general terms Goldberg (1989) inferred that both amorphous and crystalline Al^{3+} and Fe^{3+} oxide minerals play a major role in stabilising soil structure and therefore protecting clay minerals from breakdown. He suggested that Al and Fe oxides stabilise clay minerals by decreasing critical coagulation, clay dispersion, water uptake and clay swelling and by increasing microaggregation. Similar weathering processes have been postulated by other workers, eg. DeKimpe (1970) and McKeague and Brydon (1970).

Smith and Mitchell (1984) suggested that " $SiO_2-Al_2O_3-Fe_2O_3$ gel systems" are common in podzols and are usually associated with the surfaces of primary particles, and therefore suggested that even where small amounts are present they can have an

effect on soil properties incommensurate with the proportions present. Johnson and McBride (1989) also showed the presence of para- and noncrystalline materials in podzols, especially in the B horizon where the NaF test showed that this horizon had high surface reactivities. This led them to conclude that such materials would have a large influence on the chemical reactivity and physical characteristics of these soils.

3.6.2.5 Summary

From this discussion it is clear that changes in clay mineralogy relate to weathering processes over time. Differences in profile clay mineralogy between soils around Aled Isaf must therefore relate to differences in the weathering regimes found within each soil type and thus to the pedogenic processes that are occurring at the moment or which have occurred in the past. From the literature, it seems that chlorite will be the most readily weathered clay mineral from these soils, and thus the mineral most likely to give clues as to differences in the soils regimes. The products of weathering, vermiculite, HIV and amorphous materials, will also be of importance in determining what processes have occurred over time. Their presence, or absence, in a horizon will also affect what pedogenic processes can occur by masking and protecting other soil constituents. Knowledge of what products are present may also give clues as to which theory of podzolisation is the most viable.

3.6.3. Soil micromorphology (see p.295 for glossary of terms)

3.6.3.1 Introduction

Physical and chemical analyses and clay mineralogical investigations can only supply a certain amount of information about past phases of soil development and the time frame involved, and as such yield interpretations mainly concerning the parent material, the present-day status of the soil and processes which may have led to the profile characteristics visible today. They also only supply information concerning bulk samples and not the spatial arrangement of components, which micromorphology can do. Micromorphology can be used to identify relict features and interpret them in terms of past pedogenic processes and it is also possible to place such events into a relative chronological framework. This technique is used here to describe the profiles under study in an attempt to recognise features which can be interpreted in terms of past

Soil micromorphology is "concerned with the description, interpretation and, to an increasing extent, the measurement of components, features and fabrics in soils" at a scale "beyond that which can readily be seen with the naked eye" (Bullock *et al.*, 1985). This branch of pedology was pioneered by Kubiena in the late 1930's when he showed how the concept of fabric could be applied to soils and how different types of fabric could be described, classified and interpreted in terms of soil processes and soil development. By the 1980's several differing approaches to thin section description had been formulated (Kubiena, 1938; Brewer, 1964; Fitzpatrick, 1984), and in 1985 a Working Group, under the auspices of the International Society of Soil Science, produced a handbook (Bullock *et al.*, 1985) which was intended to be an internationally acceptable system for thin section description.

3.6.3.2 Micromorphology - its value and associated problems

The main principle of soil micromorphology that separates it from most other pedological techniques is that the soil is examined in an undisturbed condition such that the building elements are considered from the point of view of the way they fit together and not only as constituents or compounds. In the last 25 years micromorphology has played an increasingly important role in soil studies, for example concerning the recognition and identification of buried soils and relict features. Bullock and Murphy (1979) proposed that the inclusion of the "palaeo-argillic" horizon, identified by its micromorphology, into the classification system for England and Wales directed more attention to the field identification of soils with such horizons. This, they suggested, confirmed the belief that the palaeo-argillic horizons tended to occur where older ground surfaces had survived more recent phases of denudation, mainly outside the limits of the Devensian ice sheets. Romans and Robertson (1973) pointed out that in such horizons periglacial activity, which can have a profound mixing and destructive effect on previously developed soil morphological features, will have had a great impact, such that in most palaeosols of southern Britain cryogenic features can be detected superimposed on pre-existing morphology (*e.g.* ice wedges and fragipans; Payton, 1992; silt droplet fabrics, Macphail *et al.*, 1987). Federoff and Goldberg (1982) suggested a role for soil micromorphology here with its ability to provide information on such features not observable in the field or obtainable by bulk chemical or physical analyses.

Birkeland (1984) was of the opinion that some buried soils were easily recognisable,

although other workers (Kemp, 1985a) have suggested that their identification is difficult and rarely indisputable, the primary difficulty lying in the recognition of *in situ* horizons or pedological features, and their differentiation from transported soil materials or diagenetically altered sediments. As such, Kemp (1985a) suggested that a "microstratigraphic" approach appeared to hold considerable potential as regards the pedogenic and environmental reconstruction of both buried and non-buried soils.

Kemp (1985a) suggested that a major objective of most micromorphological studies is to interpret the composition and arrangement of soil components in terms of the particular types and sequence of processes, making it an ideal technique for the "production of feature microstratigraphies and related inferences about processes/environments, and for the isolation, ordering and interpretation of particular relict features in non-buried soils". Similar conclusions have been drawn by other workers (Bullock and Murphy, 1979; Kwaad and Mùcher, 1979; Chartres, 1980, 1984; Federoff and Goldberg, 1982; Kemp, 1983, 1985b, 1985c, 1994; Jongmans *et al.*, 1991). Macphail *et al.* (1987) and Macphail (1990) found that the study of buried soils, especially under dateable materials such as archaeological monuments, was vital to the understanding of soil development and the time scales involved. They were able to characterise agricultural activity in this way through the Holocene, interpreting concentrations of clay coatings and pore fillings, for example, as a result of former agricultural activity. Catt (1989) also used soil micromorphology to recognise relict features and suggested that argillans in soils of N.W. Europe are relict early Holocene features since the soils in which they occur are now too acidic for clay translocation. From this he questioned the dating of some soils in Southern England and Czechoslovakia as Tertiary, suggesting they may be interglacial or even Holocene.

However, micromorphology is not a magical means of solving pedological problems but simply a microscopic technique for collecting particular kinds of data on soil materials and profiles (Brewer, 1972). Having collected the data, the next step is its interpretation in terms of processes and soil history, and there are two distinct levels at which this can be attempted. The first is interpretation in terms of generalised processes, the second in terms of the chemical reactions and physical conditions of operation of the broad processes of concentration and illuviation of particular constituents. These are described in the literature (*eg.* Brewer, 1972; Bullock, 1984; Kemp, 1985a), although with many of the recognisable and well documented features it is still unclear as to their actual mode of formation. However, it is still of value to build

up a sequence of events that has affected a particular soil (and thus landscape) and this is a process adopted by most workers where possible (Crampton, 1963; Bullock and Murphy, 1979; Bullock, 1984; Chartres, 1984), although in many cases subsequent pedogenesis or sedimentary processes may totally erase pedological features, explaining their common absence in relict soils (Federoff *et al.*, 1988).

Micromorphological studies in Britain have not just been restricted to buried soils of pre-Devensian age (Kemp, 1985a). A series of soil profiles, buried around 4,000 years ago, developed in Devensian sandy materials along a palaeocatena at Woodhall Spa in Lincolnshire were micromorphologically investigated by Valentine and Dalrymple (1975). They inferred podzolisation and gleying processes from the common ferruginous grain coatings and segregations present in thin sections of the soil and interpreted the occurrence of clay coatings predating these pure ferruginous coatings as evidence for the mid-Flandrian change from clay translocation to podzolisation as the dominant soil process in many British soils. Catt (1979) proposed that this change could have been due to climate deterioration or progressive leaching and natural acidification/degeneration in a temperate humid environment.

The association of specific features in buried soils with particular environments is dependent on the correct correlation of features in non-buried soils to present environments (Pawluk, 1978). However, there is evidence from non-buried soils to indicate that similar pedological features may occur under a variety of environments, supporting the model of soil formation proposed by Cline (1962). Pawluk (1978) suggested that the problem is caused by the polygenetic nature of many soils, where some features are in non-equilibrium with the present environment, having formed at an earlier stage in the development of the soil under differing environmental conditions (ie. 'relict' features). Care must therefore be taken in relating not only buried but also surface pedological features to particular formative conditions.

A further advantage of soil micromorphology is the fact that it can be supplemented by other techniques, such as microchemical staining of components, U.V. fluorescence, SEM and electron probe microanalysis. Summaries of such techniques in relation to soil micromorphology can be found in the literature (Jenkins, 1970; Fitzpatrick, 1984).

An inherent feature associated with soil micromorphology is that of heterogeneity leading to uncertainties as to the sample size necessary to produce a representative

picture of the composition of the soil. There have, however, been relatively few statistical studies on this problem. Milfred *et al.*, (1967) presented data on the sampling density necessary for pedographic modal analysis of an argillic horizon. They concluded that to measure glaeboles, pores, papules, argillans and skeletal grains in such an horizon, with a standard error of 10% of the mean, would involve taking 21 randomly selected samples, making 2 thin sections per sample and counting 1000 points per thin section. Murphy and Banfield (1978) also concluded that a single large thin section was not enough to characterise satisfactorily the voids in a fine-textured soil.

Kwaad and Mùcher (1979) suggested that a count of 500 points/slide was viable, whilst recognising the absolute and relative errors inherent in the percentage results, although Bullock and Murphy (1979) suggested that soil material could be described as homogeneous if at a magnification of 30x all microscope fields of view (6mm) of a thin section were broadly similar with respect to all features. Murphy (1983) suggested that a count of 6000 points over an area of 25x25mm was sufficient to quantify satisfactorily the pore space of that section, although the soil is unlikely to be homogenous and therefore variability within the material needs to be assessed by comparing other randomly chosen samples (Bullock, 1984). Obviously, the less frequent a constituent of interest is the larger the sample size needed to accurately quantify it (Milfred *et al.*, 1967). In theory, vertical and horizontal slides should give similar point count values, but Conway (1980) found a discrepancy in point count values for argillans in vertical and horizontal sections, and thus there is a need to check both orientations. Voids pose additional problems. In a 30µm thick section, perfectly vertical voids will be noted down to the lowest resolution possible. However, any angle to a void and it will be seemingly reduced in size or ultimately not visible.

3.6.3.3 Micromorphological investigations of soils similar to those found on the Hiraethog Moors

Gleyed profiles.

In terms of the soils typical of the Hiraethog Moors (ironpan stagnopodzols and staghomic gleys), the available evidence is relatively scarce, although the potential for such studies to provide a wealth of information is not in doubt. Brinkman (1970) suggested that a process termed ferrolysis, as described in section 3.6.1.1, was a major genetic process in many pseudogley soils of Europe. Brinkman *et al.* (1973) also

suggested that under such conditions birefringent argillans were altered to isotropic, characteristically grainy cutans by this process, whereby silica liberated from smectite and illite was reprecipitated as microcrystalline quartz and the argillans were residually enriched in anatase and kandite.

An understanding of gley morphology has been helped by simulation experiments such as those of Yarılova *et al.* (1985). They showed that although gleying did not seem to alter the general features of the microfabric it did bleach the plasma due to a loss of most of the ferric iron hydroxides. It also gave rise to other features, such as microzones from which fine-grained material had been washed out, disintegration and compaction and the formation of organo- mineral compounds.

Bouma *et al.* (1988) suggested that periodic or permanent saturation with water will create oxidising and/or reducing conditions which will have a profound impact on soil physical, chemical and biological processes, and proposed that micromorphological analyses are of particular use here to show the effects of this on a microscale. They also suggested that surface-water and groundwater gley phenomena may be distinguished by the characteristic precipitation and leaching compounds which may result, especially between Fe and Mn, from differences in a substance's redox characteristics. Ponnampertuma (1972) reviewed the redox reactions of iron and manganese in waterlogged soils and suggested that up to 50% of the free iron oxides present in a soil may be reduced within a few weeks of the soil becoming totally waterlogged, and that the lower the initial degree of crystallinity of the iron the higher the reduction percentage. He suggested that, since Fe(II) is oxidised at a lower Eh than Mn(II), as a soil aerates Fe(II) is rapidly converted to Fe(III) oxide hydrates. These precipitates may then sorb Mn^{2+} or form co-precipitates to give stains, nodules and concretions whose composition will therefore reflect the nature of the environment in which they were formed. Electroprobe microanalysis is very useful here, and often reveals the zoned nature of such deposits suggesting a cyclic mode of formation.

Podzolic profiles

The use of soil micromorphology in the understanding of soil developmental processes in podzols goes back to the work carried out by Crampton in 1963, around which time the first micromorphological criteria for spodic and cambic horizons were being proposed by the USDA (1960, 1964, 1967; summarised in Claydon, 1970). Crampton

(1963) described the micromorphology of ironpan stagnopodzols developed on Silurian shales, noting the higher silt content of the upper mineral horizon and the highly porous nature of the B_s. He suggested that the B_f in such soils was less pervious than that of similar soils developed on Carboniferous and Old Red Sandstone rocks because of the smaller grain size of the parent material. He also noted a brown staining of shale fragments in the B_s which he suggested was due to oxidising conditions, and suggested that such oxidising conditions were also at one time present in the surface mineral horizon (E_{ag}), but that these had been replaced subsequently by reducing conditions since rock fragments in this upper horizon had brown-stained cores surrounded by grey rims. Macphail *et al.* (1987) suggested that the stage of stone rim bleaching on small stones in the surface layers of Scottish soils buried below Neolithic house walls, lynchets and in the final profile developed on upslope field surfaces demonstrated a sequence of profile development from acid-brown soil to the present-day peaty-gleyed podzol.

The first major review of work carried out on podzolic B horizons was that of Claydon (1970) on podzolised brown earths, in which he included the Manod Series. He confirmed that the micromorphologies of the soils studied could be placed into one of two categories as set out by the USDA. In the first the fabric was composed of loosely aggregated, very fine primary peds *ie.* highly vughy, intertextic fabric composed of very fine, rounded blocky primary peds closely resembling the diagnostic fabric of crumbly spodic horizons, with the s-matrix being characteristically silasepic (Bullock *et al.*, 1985, Table 5.1). The second lacked the very fine primary peds and had a denser porphyroskeletal fabric, classified on micromorphological grounds as a cambic horizon.

There has been an emphasis on grain coatings in the classification by morphology of podzols, and this probably stems from the fact that many podzols studied are developed on coarse-textured materials with little fine material to fill the intergranular spaces. However, Mackney and Burnham (1964) suggested that podzols formed in fine-textured materials will have B_s horizons with a microfabric consisting predominantly of fine shot-like peds, in places weakly aggregated into crumbs, and that unorientated grain coatings were a subordinate diagnostic feature.

Claydon (1970) noted that peds of the first type may be linked to adjacent peds by paler yellow-brown material attached to all or part of their margins, and similar linking material had been noted by Mackney and Burnham (1964). Aristovskaya (1958, 1963),

in a study of certain Russian podzolic soils, showed that certain protozoa, feeding on bacteria associated with humus complexes, accumulate iron in their cells which may become surrounded by a gel of iron hydroxide. Given enough time and sufficient protozoa, it was suggested that former animal cells could have acted as foci for the pellet-like primary peds and that the yellow-brown linking material may be an aureole of iron hydroxide gel or a gum secreted by the cells.

Farmer *et al.* (1985) also noted the presence of similar pale yellow coatings and suggested, from analyses carried out using the electron microprobe, that they were composed of allophane. They described allophane coatings in the upper Bs as translucent, pale yellow, strongly auto-U.V.-fluorescent, gelatinous deposits, locally stained dark brown as detailed in section 3.6.1.2 and suggested that the allophane was deposited from migrating solutions containing hydroxyaluminium orthosilicate (proto-imogolite) sols, and not formed *in situ* from precipitated organic complexes. Cruickshank *et al.* (1988) carried out a similar study on the nature and origin of amorphous coatings in albic and spodic horizons, again showing domination by Si, Al and Fe (Si:Al ratios of 1:3), with Fe-rich and Al-rich coatings forming zonally distinct subparallel phases.

de Bakker and Schelling (1966) proposed that the pellet-like peds found in B horizons were very similar to micro-arthropod droppings of moder humus, micro-arthropods having now been shown to play an important role in the structural development of, at least, surface horizons (Pawluk, 1985). However, moder humus pellets differ in being black, lacking inclusions of identifiable grains and being without the distinctive yellow-brown linking plasma, and as such Claydon (1970) had earlier concluded that this was not the origin of the fabric. However, Sanborn and Lavkulich (1989b) suggested a faunal origin for some B fabrics they studied from Coastal British Columbia which were complexes of spongy, crumb and subangular blocky microstructures. They divided coatings from the B_s of ferro-humic podzols of into two types of amorphous organic matter: (i) polymorphic, forming discontinuous masses of variable colour and density (ii) monomorphic, consisting of masses of uniform colour and density, and showed these latter to be areas of metal accumulation (Al, K, Ca, Fe and Zn). It is likely that these dominant coatings differ considerably from those noted by Claydon (1970), although Sanborn and Lavkulich (1989a) suggested that some of the palest yellow zones may be allophanic in nature from chemical analyses of bulk samples.

De Coninck (1980), in a review of the major mechanisms of formation of spodic horizons, described the structure of spodic horizons as ranging from loose, with many roots, to very cemented with few roots, and suggested that these differences could be related to changes in microstructure. He described loose spodic horizons as having a predominance of polymorphic pellets and aggregates, suggesting that their formation was due to biological activity since there were pedotubules, high numbers of roots, thorough mixing of organic units with clay and silt, and a relatively young mean residence time (MRT) of the organic matter. Cemented horizons, he noted, were dominated by organans or monomorphic coatings which he suggested were more consistent with organo-mineral compounds immobilised in a gel-state, *ie.* the coatings were strongly cracked indicating the transition of a gel into a solid, they contained much Al or Al+Fe but little Si and the MRT's were considerably higher than in the loose horizons. Page and Guillet (1991) give a similar account of loose and cemented horizons, stating that loose Bs horizons may have MRT's of 500 years whilst the more cemented horizons may have MRT's of 800 years and higher C:N ratios.

In more general terms Maltby and Caseldine (1982) studied soil development on Bodmin Moor, comparing present-day soil morphologies with those of soils buried beneath Bronze Age barrows. They suggested that there was direct pedological and palaeoecological evidence to support the theory that brown soils existed in pre-Bronze Age times in south-western England at a site subsequently developing an ironpan and accumulating a strongly acid peaty surface. Their evidence was based on chemical criteria which suggested that the buried soil had a closer affinity with brown soils than with the present-day stagnopodzols. Also, the presence of infilled channels, which often bifurcated and contained possible earthworm casts, and an absence of a highly acidic peat or mor humus surface necessarily implied such affinities. They gave a date close to 1,560 bc (^{14}C dates for barrow construction) for the loss of worms since some, but not all, casts extended up into the barrow. This they compared with an experimental earthwork on Overton Down constructed in 1960, where worm casts were recorded in interstitial spaces throughout the experimental bank within 4 years of its construction. West *et al.* (1991) studied present-day effects of earthworm activity on soil microfabric, and showed that their activity orientated clay domains into a porostriated b-fabric adjacent to the earthworm channel, as well as resulting in some general compaction of the soil adjacent to channels, another feature also described for the buried soils studied by Maltby and Caseldine (1982).

Björkhem and Jongerijs (1988) have also suggested a biogenic origin for the porous and crumbly nature of the B_s horizons they studied, as well as for more coalesced aggregates, suggesting that this was a feature of the ageing of the excrement. However, they suggested that even in soils showing a high activity of burrowing animals, such as earthworms, podzolisation may occur, and they suggested that such aggregates can be formed *in situ* in B horizons of podzols.

It is, nevertheless, important to remember that such soil changes are not necessarily synchronous even over short distances. The effects of aspect, subtle differences in elevation, gradient and hydrology, together with any differential influences of prehistoric land management, should not be ignored as causes of significant delays in the processes of conversion of brown soils to ironpan stagnopodzols. It must also be remembered that it is difficult to directly compare micromorphologies of soils, since differences in parent material and texture, for example, can lead to differences in micromorphologies (Righi, 1987).

In many such studies man is implicated in the changes that are suggested for soils, with much of the evidence coming from micromorphological studies of soils buried beneath archaeological sites as compared to the present-day soils. Scaife and Macphail (1983) noted characteristics of argillic subsoil fabrics from two Mesolithic sites at Selmeston and High Rocks which exhibited primary limpid, micro-laminated clay coatings characterised by fairly high birefringence, which were succeeded by larger amounts of dusty impure clay. They suggested that the later "coarse-grained" illuvial phase was related to Mesolithic activity, possibly opening up the forest canopy leading to increased windshake of trees or some other form of anthropogenic disturbance. Macphail (1986) has also associated instances of early soil erosion, the occurrence of bleached sand, and the initiation of peat formation in upland areas of Dartmoor and the Pennines with the activity of Mesolithic man.

Romans and Robertson (1983) proposed that differences in the distribution patterns of textural pedofeatures are related to cultivation and to the type of cultivating implement used. They also suggested that Neolithic cultivation may have been responsible for the physical breakdown of surface soil horizons whose content of stabilising organic matter was already low, so that the resulting soil debris was readily mobilised by soil water. Claydon (1977) suggested that the dramatic effects of climatic deterioration at the beginning of the Iron Age (Sub-Atlantic climatic period) were superimposed on a

system already adversely altered by man.

Macphail *et al.* (1987) proposed that over many upland regions of Britain, brown soils were still present as late as Bronze Age times, but suggested that during the Bronze Age the cumulative pressure of anthropogenic activities led to the large-scale podzolisation of these areas. Keeley (1982) suggested that the expansion of Iron Age and Roman agriculture onto marginal areas such as Dartmoor and the Pennines led to soil acidification, podzolisation, gleying and peat formation.

3.6.3.4 Summary

It appears from the previous discussion that there are still many micromorphological features of stagnohumic gley soils and ironpan stagnopodzols that cannot be fully explained. Of particular interest to this research is the fabric of the B horizon (spongy or compacted) and the formative agents for these differing fabrics. If, as is widely suggested, the loose friable B_s fabric has a biological origin then this has very important implications for previous soil phases. The formation of the cemented B_f horizon is central to an understanding of the development of these soils, and a better understanding of this will be of great value. Clay movement and redeposition is another feature commonly described for such soils, and is thought to relate to a previous pedogenic phase. If these can be identified and analysed further information may be gained concerning the process itself and the conditions during this phase of soil development.

Chapter 4. Holocene Environmental History

4.1. Introduction

The previous chapter has dealt with the literature concerning present-day physical and chemical soil regimes and possible phases of past soil development. This obviously leads to inferences being made about past environmental conditions, and the effects these may have had on pedogenic processes. However, there are more precise means of interpreting past environments, namely the use of micro-fossils, especially where they have accumulated in a stratigraphic sequence that exhibits temporal order, such as peats, lacustrine sediments and certain soil organic layers. Hiraethog is an ideal location for such studies due to an abundance of these materials. This part of the research was therefore carried out with the aim of reconstructing past vegetation communities on Hiraethog and from this inferring past environmental conditions, especially those that would have influenced pedogenesis. The aim was also to place such changes in a relative and/or absolute time framework so that comparisons with other sites and existing archaeological data could be made.

Pollen analysis has been the main technique utilised to reconstruct past vegetation changes with supplementary information coming from an analysis of charcoal fragments in the samples, and an attempt was made to use bioliths to study other environmental factors. Plant macrofossils were also extracted and analysed, but due to time constraints this could not form a significant part of this research. Tephrochronology has shown much potential elsewhere to provide information concerning the Holocene, and so a study of this was initiated. A time framework for the environmental history was provided by radiocarbon dating (^{14}C) utilising both radiometric and AMS techniques. It was intended that this data from the Hiraethog Moors would be linked with palaeoenvironmental evidence from soils to facilitate the understanding of Holocene landscape development in upland areas.

4.2 Palynology

Palynology covers the study of the biological components concentrated through standard preparation techniques, and includes both pollen grains from higher plants and spores from cryptogams. Their small size and highly recognisable structures and sculpturing are useful in the study of past conditions. The latter allows identification to, in some cases, species level although problems are caused by their small size since this

means that, although the pollen in a sediment is derived from a wide area, it is often difficult to know exactly the pollen catchment for a particular sediment (Moore *et al.*, 1991).

Pollen grains and spores are generally best preserved where the environment in which they lie is acidic. Pollen grains and spores are preserved more readily than other plant parts due to their structural chemistry. The wall is made up of two layers; exine in the outer layer (composed of sporopollenin) and an inner layer of intine, very similar in construction to an ordinary cellulose cell wall. Faegri and Iversen (1989) give a detailed account of pollen wall structure and terminology. This resistant wall is thought to be needed primarily to avoid desiccation during the aerial journey, but no real explanation has been put forward to explain the elaborate and distinctive sculpture that is found, nor the enormous range of sculpturing types so useful to the pollen analyst (Moore *et al.*, 1991). However, pollen grains occur in great abundance in sediments and this allows a quantitative recording of the various pollen types to be made. As such palynology has proved extremely useful to many branches of science, such as those tracing the history of plant groups and species; those tracing the history of plant communities and hence habitats; those dating deposits; those studying climatic history, and those following the course of mans influence upon the environment.

4.2.1 Sediments in which pollen grains and spores are preserved

Although the coat of pollen grains and spores is relatively resistant to decay, it is by no means "non-biodegradable". Some small invertebrate animals appear to ingest pollen grains leading to their degradation, and micro-organisms are also capable of degrading pollen under aerobic conditions at neutral pH (Moore *et al.*, 1991). As such, anaerobic, waterlogged and acidic deposits are the most valuable in terms of pollen preservation; this usually means peats and lacustrine sediments.

Attempts have been made to carry out palynological investigations of soils (Dimbleby, 1962; 1985), although there are many problems associated with this, such as faunal mixing, aerobism and high pH; Moore *et al.* (1991) suggest that there is virtually no pollen preservation in soils at a pH level of >6. Consequently it is now considered to be of little value, except when applied to mor or peaty surface horizons and buried soils (R. Tipping, pers. comm. 1994). However, when studying buried soils, the stratification of pollen within the soil is of less interest than the overall pollen composition, and under

these circumstances the difficulties associated with pollen redistribution are therefore less important (Moore *et al.*, 1991).

Peats and lacustrine sediments are more suited for palynological investigations since they have usually developed in a stratified sequence and, assuming no or minimal disturbance, a vertical series of samples will exhibit strict temporal order (Moore *et al.*, 1991). It is unlikely that this sequence will become inverted unless severe erosional/depositional events occur. Clymo's (1973) studies indicated that a compact layer of peat often forms by a depth of 5-10cm, and as such mixing of pollen within the surface layers of peat is likely to be limited. Iversen (1969) also concluded that mixing at the surface, as shown by charcoal, was not significant in cores taken from Draved Forest. However, since 10cm of peat can easily become compacted into a vertical space of 1cm or less lower in the profile, such mixing effects will be lost (Moore *et al.*, 1991).

These effects may be more of a problem in lacustrine sediments. It is generally accepted that such sediments are mixed prior to final sedimentation and a single sample is therefore more likely to represent the average of several, rather than the current, years input. Further difficulties arise due to water turbulence and the reworking of older sediments from banks and shallows, although many of these problems can be overcome by sampling lakes at the deepest point (Jacobson and Bradshaw, 1981).

A useful indication of the rate of organic matter accumulation is the degree of humification exhibited by the material. Granlund (1932) concluded that strongly humified peat was formed in periods with a low peat accumulation rate, while less well decomposed peat originated in periods with rapid peat growth. This has allowed inferences about past climates to be made since low precipitation rates, which gives rise to a vegetation of less water demanding species and to greater oxidation of the upper peat layers resulting in the formation of "recurrence surfaces", is considered the main cause of strong humification. This has been studied in detail across North-west Europe, for example at Bolton Fell Moss and Walton Moss in North Cumbria (Barber *et al.*, 1994). The degree of humification can be determined subjectively, although exact values can be determined using a chemical-optical method as outlined in Aaby (1986) and Blackford and Chambers (1993).

4.2.2 Holocene vegetational history

Table 4.1 gives a generalised view of changing climatic and archaeological periods for N.W. Europe over the Devensian Late-glacial/Holocene, climatic information being deduced from the changing vegetation communities inferred from the study of different fossil types. As can be seen the Holocene, that period 10,000 years BP to the present-day, has seen changes in vegetation, climate and the human population and culture and it is now realised that the effects each of these factors has had are interrelated and very difficult to separate.

Table 4.1 Generalised Devensian Late-glacial/Holocene vegetational, environmental and archaeological changes in the British Isles. Adapted from Addison *et al.* (1990), Manley *et al.* (1991), Moore *et al.* (1991), and Bell and Walker (1992).

Years BP	Pollen zone (Godwin)	Climatic Period (Blytt/Sernander)	Climate	Archaeological period
1000				Historic
				Roman
2000	VIII	Sub-Atlantic	Deterioration	Iron Age
3000				Bronze Age
4000	VIIb	Sub-Boreal	Climatic optimum	
5000				••• Neolithic
6000	VIIa	Atlantic		Rapid amelioration
7000				
8000	VI	Boreal		
9000	V		Cold	
10000	IV	Pre-Boreal		
	III	Younger Dryas		
11000	II	Allerød	Rapid amelioration	Late-glacial
12000				
13000	I	Older Dryas		
14000				
15000	End of Late Devensian glaciation			

••• Elm decline

Godwin (1940), from detailed analysis of pollen records, proposed that the last 10,000 years could be divided up roughly into three climatic types; increasing warmth, maximum warmth and decreasing warmth, as shown by the pollen curves for tree species such as birch, pine, elm, oak and lime. He suggested a zoning system for vegetational changes that had occurred since the Younger Dryas, creating 8 zones, some with sub-zones, and this system has frequently been used to correlate data from different sites (Turner, 1962; Hicks, 1971; Evans and Walker, 1977). Below is a summary of the general vegetation changes which have occurred over the Holocene in the British Isles, adapted from Watkins (1991) and Bell and Walker (1992). Following this, some of the changes which are thought to have relevance to the study area, the Hiraethog Moors, will be discussed in more detail.

The rapid climatic amelioration between 10.3 and 10ka BP is thought to have led to changes in the vegetation of Europe, with tundra being replaced by open grassland and then by *Juniperus*, *Salix* and *Betula* dwarf shrub heath, with *Juniperus*, which is shade intolerant, rapidly being replaced by *Betula-Corylus* woodland. Because of the diverse herbaceous communities present at this time it is likely that tree cover was fairly sparse.

The period 9-5ka BP was characterised by the immigration and expansion of temperate deciduous trees which formed dense mixed woodland dominated by *Corylus*, *Quercus*, *Ulmus* and *Tilia*, reducing herbaceous cover and the fern understorey. By 8ka BP *Quercus* and *Ulmus* had expanded across much of the British Isles, followed by *Alnus* between 8-7ka BP and, between 6-5ka BP, *Fraxinus*. It is thought that *Alnus* probably replaced *Salix*, *Betula* and *Pinus* on damp and waterlogged sites and may have heralded a shift to wetter climatic conditions which appear to have begun around 7ka BP.

From 5ka BP onwards, British vegetation patterns were disrupted and a retrogressive sequence of vegetational changes resulted in the progressive replacement of deciduous woodland by an incompletely forested landscape with heaths, extensive grasslands and, particularly in upland regions, blanket mires. Such changes become increasingly difficult to interpret because of the widespread evidence for an anthropogenic impact on the landscape.

However, there was a climatic shift to wetter conditions which became particularly marked after 2.5ka BP, and in the period 6ka BP to present-day, *Ulmus*, *Tilia* and *Corylus* were replaced progressively by *Quercus* and *Betula*, whilst in the uplands

extensive blanket mire development led to a progressive fall in tree-line altitudes. By 4ka BP it is thought that the upland regions of the maritime fringes of north-west Europe were essentially treeless, and covered largely by acidophilous heathland, grassland and ombrogenous blanket mire. The elm decline is thought to have begun in Wales around 5ka BP, and by 3ka BP man is assumed to have had a marked impact on the landscape with the appearance of *Plantago*, Caryophyllaceae and *Rumex*, as well as the first recorded cereal pollen. This phase is usually associated with an increase in inorganic sedimentation due to an increase in erosion arising from arable farming practices.

It is thought that, following the elm decline, clearance took place on an ever increasing scale, eventually resulting in the present largely deforested "cultural landscape" of Europe, and it seems that a sequence of woodland clearance to open landscapes occurred over much of upland Britain, with the actual timing of the event depending on local conditions. One area extensively studied is Dartmoor in the south-west of England where it is proposed that by 3.5ka BP, when monument construction dominated, the landscape was becoming increasingly open as a result of grazing and regular burning. Around 3.5ka BP, in a time of accelerated clearance to a scrubby grassland, the construction of stone boundary walls, or "reaves", which delimit territory on the periphery of the moor occurred. It is suggested that at this time some areas had already begun to develop podzolic soils and that the onset of soil deterioration was the cause of concern over land ownership, although this may also have been augmented by the local occurrence of tin which may explain the greater Bronze Age impact on Dartmoor as compared to other areas such as Exmoor and the North York Moors, where extensive clearance did not occur until Iron Age times.

The fluctuating use of moorland in both the Bronze Age and the Medieval episodes, characterised by more intense use, may partly relate to climatic factors, these periods being warmer and drier than the intervening and succeeding periods. Ellis and Matthews (1984) studied podzol development in an arctic-alpine environment and suggested, from ¹⁴C dates, that the surface organic horizon began to accumulate about 4,500 BP, with a major episode of organic matter illuviation commencing soon after this time. They proposed that this was initiated by a deterioration in the climate, but that land-use pressure may also have been a factor along with social considerations. It is possible that, principally as a consequence of human activity, areas such as Dartmoor became increasingly marginal and unable to support long-term intensive settlement and

occupation, and as such were set aside for more specific forms of exploitation, such as grazing, based on settlements beyond the moor. The present-day vegetation is therefore, to a large extent, a reflection of these regimes.

4.2.3 The alder rise

Watkins (1991), from comparisons of radiocarbon dates quoted in the literature, suggested that the empirical limit of *Alnus* in North Wales ranged from 7,000 BP to 8,900 BP. Smith and Pilcher (1973) had earlier suggested that the timing of the alder rise varied by about 2,000 years across Britain and Ireland. Initially, it was suggested that alder spread across Britain moving from south-eastern England (Huntley and Birks, 1983). However, data presented by Chambers and Price (1985) for a Welsh site (Moel y Gerddi) suggested that a spread of alder into Britain from the west needed to be seriously considered as an alternative to the south-eastern route. Explanations put forward to account for these discrepancies included an alder rise due to the expansion of populations already present in Britain at the beginning of the Holocene (Bush and Hall, 1987) or that alder may have survived the last cold stage within the British Isles and increased in response to disturbances. Birks (1989) suggested that the peculiar ecological requirements of alder would have led to a multiplicity of explanations for the alder rise.

Alder is a tree of wet, mildly basic habitats, and its distribution will have been primarily limited by soil moisture. Alder can occur as pure stands or mixed with other species such as *Fraxinus*, *Salix*, *Betula*, *Quercus* and *Ulmus* depending on local site conditions. In a further review of the Holocene alder spread Bennett and Birks (1990) suggested that maps of alder communities over time did not show any pattern that could be described as spatially coherent, and so found it impossible to suggest any time-transgressive spread in any direction across the British Isles. Its spread is much more erratic in space and time than any other tree in the British Isles for which there is adequate data.

The combination of sporadically increasing areas of suitable habitat and temporally intermittent conditions for reproduction resulted in a pattern of spread and increase during the early and mid-Holocene across the British Isles that is, for all practical purposes, random at these spatial and temporal scales. Watkins (1990) gives dates around 7,500BP for the alder rise on the Arfon Platform, whilst Chambers and Price

(1985) suggest an even earlier date of 8,000BP for a valley mire site on the west coast of Wales.

4.2.4 The Elm Decline

The decline of elm across N.W. Europe has received much attention and several causes have been suggested to account for its occurrence and timing. Britain, as compared to Scandinavian countries, had a more oceanic climate and so it was thought unlikely that a critical threshold of temperature was crossed by the climate change separating the Atlantic from the Sub-Boreal. Pennington (1969) suggested that, although in Denmark the Elm decline was associated with a decline in ivy and mistletoe, two frost sensitive plants, in Britain no such associated decline was noticeable. Also, as elm declined, ash began to appear which, like elm, is demanding in its soil requirements and a good indicator of an opening up of the forest since it is light demanding. It was therefore thought unlikely that soil deterioration was the cause of the decline in elm, a decline seen right across N.W. Europe, all dated to within a century or two (Hirons and Edwards, 1986). Huntley and Birks (1983) concluded that the overall geographical pattern and chronological spread of the elm decline did not easily fit any climatic hypothesis such as greater coolness, wetness or continentality, especially since the decline appeared to have been most pronounced in the west.

Troels-Smith (1960) and Turner (1962; 1964) suggested that man may have used elm leaves as animal fodder, a practice noted today in areas such as the Caucasus and the Himalayas (Pennington, 1969). Pollarding every 2-3 years is thought to be able to prevent flowering (Smith, 1981) and since elm leaves are nutritious they would have provided an important source of fodder for pioneer animal husbandry in the densely wooded landscape of north-west Europe. Turner (1962), therefore, proposed that the boundary between Godwins (1940) Zones VIIa and VIIb should now be ascribed to interference by man rather than, as previously, to climate .

Further evidence to support mans role in the decline of elm came from Denmark where a technique was used in which large numbers of pollen grains were counted in very closely spaced samples. Iversen (1964) carried out one such study in Draved Forest in Southern Jutland and found that as elm declined, so Ribwort Plantain (*Plantago lanceolata*) made its first appearance, a plant thought to be characteristic of pastures and waysides. The association between the elm decline and human activity is often

made because of the increase in such anthropogenic indicator species at the time of the elm decline. Iversen (1964), who named the shifting cultivation which took place around this time "Landnam clearance", gives examples of a decline in total tree pollen associated with an increase of weed pollen from perennial species such as *Plantago lanceolata*, *Rumex*, *Artemisia* and members of the Chenopodiaceae. Behre (1981; 1986) described the use of anthropogenic indicator species, citing cultivated plants such as cereals, as well as what he considers to be the most important indicator, *Plantago lanceolata*. This plant is favoured by cultivation which will rip up soil but not actually destroy plant perennating organs. However, he recognised that plantains may indicate pastoralism as well as arable farming, and so supported the use of an arable/pasture index, first proposed by Turner (1964), whereby Cerealia, Compositae, *Polygonum* spp and *Trifolium*-type were selected as arable indicators and *Plantago lanceolata*, *Rumex acetosa/acetosella*-type, *Ranunculus* spp. and *Bellis*-type as indicators of pasture.

Groenman-van Waateringe (1983; 1988), however, suggested that the link between pollen from plants indicative of agricultural activity and the elm decline may be partly illusory. He proposed that in a completely wooded landscape small scale clearances are likely to be masked unless they occurred very close to the site of pollen deposition, whilst under more open conditions following elm decline, these clearances would be more likely to register in pollen diagrams. Bell and Walker (1992) suggested that this effect may have been amplified if human groups were specifically attracted to more open areas on better soils where the elm had previously been growing.

Recent detailed pollen studies of the elm decline horizon show that it sometimes occurs following a series of human impacts, such as at Pawlaw Mire in Northumberland (Sturloditter and Turner, 1985) and the Isle of Wight (Scaife, 1988). Hirons and Edwards (1986) suggested, from pollen evidence from Ireland, that the reduction in elm could be related to human activity, but thought that there was still a possibility of a concomitant disease explanation. Also, from their evidence, they could not eliminate a contribution from climatic change although they thought that this would have had to have been temporary in view of a subsequent restoration of elm levels and thus suggested that this was unlikely.

However, Bell and Walker (1992) proposed that all anthropogenic explanations for elm decline suffered from a "fatal flaw" in that they fail to take into account the scale of the

event since Rackham (1980) had suggested that elm made up about 1/8 of the woodland of Britain covering, in aggregate, some 10 million acres. Bell and Walker (1992) concluded that this "opened up the possibility that the areas most intensely settled by early farming communities \approx 5,000 BP may have been partly determined by those areas where disease had created sufficient ready-made openings in the forest. Human activity would have aided the spread of the disease since, in contemporary outbreaks, trees damaged by stock or pollarding were especially susceptible to infection". Hence, they suggested that a "disease hypothesis acknowledged the scale of the phenomenon whilst at the same time explaining its general contemporaneity with the spread of farming." Bell and Walker (1992) proposed that this disease hypothesis is strengthened by the discovery of fragments of beetle *Scolytus scolytus* in horizons immediately below the elm decline in a peat sequence at the Mesolithic site at Hampstead Heath, London and of wood damaged by another *Scolytus* species at Åmosen, Denmark.

From this it can be seen that the elm decline in European vegetation diagrams at about 5,000 BP has been attributed variously to climatic deterioration, human influence and disease, factors which have all been discussed individually as *the* cause. Possible synergistic effects had, until recently, been neglected, and so had additional, but less obvious causes like increased virulence (mutations) of pathogens, dispersal of pathogens and/or vectors.

4.2.5 Blanket peat initiation

Another major vegetational change is that of the formation of blanket peat. Almost all areas covered by blanket bog are thought to have once carried woodland (Bell and Walker, 1992), as shown by the presence of tree stumps at the junction between the underlying mineral soil and peat, noted in this instance around the margins of the Aled Isaf reservoir. Opinion is divided as to the cause of this change, and it is suggested that this is a classic illustration of the "equifinality problem" *ie.* several causes resulting in the same final feature (Bell and Walker, 1992). Godwin (1975) suggested a climatic cause, pointing to sites in Britain where peats started to form about 7,000 BP (Early Atlantic) and 3,000 BP (Early Sub-Atlantic), both episodes of increased wetness. However, Smith (1981) suggested that, as the number of sites with radiocarbon dates for peat initiation has increased, so it is becoming clear that peat initiation occurred over a more protracted period.

Smith and Taylor (1969), Pennington *et al.* (1972) and Taylor (1980) have suggested natural pedogenic processes as a cause, with the gradual acidification of soils leading to a build up of a mor humus and peat, suggesting that in some Scottish and Irish sites this was underway before significant human impact in the Bronze Age. However, there are many examples where peat initiation seems to coincide with Neolithic or Bronze Age activity (Lynch, 1981; Smith, 1981; Wiltshire and Moore, 1983; Mitchell, 1989; Cruise, 1990; O'Connell, 1990), and Bell and Walker (1992) therefore suggested that there seems to be "general agreement that in some high rainfall areas...peat formation was underway before human activity began on any scale, and so may therefore have been the result of natural Holocene conditions". They suggested that in other areas there is "considerable evidence for human activity, albeit often on a small scale, at the critical soil/peat interface and it seems that people played a key role in tipping the ecological balance towards peat inception. The result may be that in some areas a process which would have happened much later in the present interglacial was greatly accelerated by human activity, whilst elsewhere the area covered by blanket peat may have been extended by the ecological changes which people brought about".

4.2.6 Palynological evidence from the Hiraethog Moors

Evidence in support of human activity affecting vegetation in the uplands of Clwyd is presented by Hibbert (1993) from peat samples and buried soils recovered in connection with the Brenig Valley excavations. These results indicated that during the Mesolithic *Alnus* and *Betula* were growing at the site (300m O.D.), with *Quercus*, *Ulmus* and *Tilia* pollen possibly derived from lower altitudes in the valleys of the Clwyd, Conwy and Dee. There is little reported evidence of an Elm decline, but Hibbert (1993) suggested that this may not have been detectable if the pollen was being produced some distance away. However, there is evidence of *Plantago* and *Rumex*, which he thought may represent the upgrading of parts of the moors to support sheep or cattle, possibly by the late Neolithic. Hibbert (1993) suggested that the expansion of grasses and ericaceae occurred around 2,000-1,500 bc, the period of the development of the Brenig cemetery.

Evidence from buried soils gave a similar picture, and was taken to indicate the environment at the time that man was active in erecting the monuments. Such analyses showed low tree pollen percentages, suggesting that monument construction took place during the Late Neolithic/Early Bronze Age when the climate was relatively dry and

warm, before a general deterioration took place leading to an advance of heather moorland. However, an interesting point is that turves making up the monument contain higher heather pollen values than the underlying turves, and this was interpreted as the result of turves having been carried in from elsewhere, perhaps from fields being cut out of the heather in the southern end of the valley. Deposition of peat, however, ends at this site as *Fagus*, *Tilia* and *Carpinus* become part of the pollen rain, and Hibbert (1993), in comparisons with dated sequences from similar environments, proposed that this occurred during the Romano-British time, perhaps during the third to sixth centuries A.D.

4.2.7 Summary

The Holocene has seen changes in vegetation across the British Isles which require climatic alteration or human impact for their interpretation. Overall, the effect of humans on the development of vegetation was originally regarded as being of minor importance in the interpretation of pollen-analytical data because no pollen analytical technique was then known with which to assess such effects. Other environmental factors (climate and soil) were thought to have dominated the post-glacial vegetation development, at any rate in N.W. Europe, although it is now thought that human activity was, at least in part, the cause of many of the Holocene vegetation changes that occurred. However, it must be remembered that the causes of vegetation changes registered in a pollen diagram may be general or local, or usually general causes modified by local conditions, and that these need to be taken into account in any interpretations of pollen sequences. Also, the result of human impact or climatic change can be the same, and so distinguishing the two in pollen analytical data can often only be tentative.

4.3 Charcoal

Patterson *et al.* (1987) have suggested that charcoal preserved in lake sediments, peat and soils provides a record of past fire occurrence, and that an understanding of fire history is important in evaluating interactions between vegetation, climate and human disturbances. The role of fire in vegetational change and its effects on ecosystems has been well documented (Slaughter *et al.*, 1971; Wright and Heinselman, 1973; Wein and Maclean, 1983), and very often the use of fire by humans is inferred in such studies (Iversen, 1964; 1969).

4.3.1 Problems of analysis

Unlike pollen, which is produced fairly consistently over time, charcoal is produced in large quantities at irregular intervals, depending on the specific site characteristics and, therefore, theoretically individual events can be recognised from an analysis of charcoal particles extracted from sediment cores. However, the quantity of charcoal finally counted is dependant on a number of factors; on taphonomic processes, on redeposition and mixing of particles at the site of deposition and on the sampling regime used (Patterson *et al.*, 1987).

Taphonomic processes, *i.e.* those acting on an object from the point at which it is produced to the point where it is finally sampled (Webb and McAndrews, 1976), include charcoal dispersal (usually by wind and/or water), the dispersal time and the deposition processes. These processes are all discussed in detail by Patterson *et al.* (1987), who present theoretical models for charcoal dispersal to predict the quantity and size of charcoal particles that could be expected at increasing distance from the fire source under both calm conditions and under the influence of a unidirectional wind. Such models highlight the large number of variables involved but are highly idealised (Watkins, 1991).

As with pollen, since a compact layer of peat often forms by a depth of 5-10cm, it is suggested (Iversen, 1969; Clymo, 1973) that mixing of charcoal in a peat core is not a problem. However, Patterson *et al.* (1987) recognised that trampling by large animals, frost heave and human activity can all lead to some mixing, the levels of which will vary between sites.

The importance of sampling intensity and sediment accumulation rate must also be taken into account, especially in the identification of instantaneous events such as fires. Patterson *et al.* (1987), for example, suggested that where sample thickness represents 10-20 years and when contiguous samples are not counted, fires may be totally missed. By contrast, if a sample represents 100-200 years, several fires could be represented or a narrow band of charcoal from a single fire could be averaged with adjacent deposits with little charcoal. The resultant estimate of charcoal concentration would be low and the single fire would go undetected. In each case, fire frequency determines whether or not fires will be detected under given conditions of sampling depth and interval, and accumulation rate. Patterson *et al.* (1987) therefore suggested that contiguous, perhaps

high resolution sampling is a necessity in order to pick up essentially discrete fire events.

There are various methods which are used to quantify charcoal which may be broadly divided into those that use the microscope and those that attempt to measure elemental carbon. Watkins (1991) attempted two methods, microscopic identification and digestion/combustion, but found the latter to be time consuming, thus giving poor resolution, and that replicate samples produced results with large errors making it difficult to establish the significance of particular trends, and therefore this method was deemed to be unsuitable. Other available methods include image analysis, electron microscopy, spectrographic analysis and magnetic susceptibility, which are all discussed in detail by Patterson *et al.* (1987). Since charcoal analysis was not attempted until the end of this research project it was therefore decided to count charcoal fragments on the previously prepared slides used for pollen analysis.

One of the main problems with this technique is that of charcoal identification (Patterson *et al.*, 1987). Samples usually contain jet black, opaque, angular particles that are clearly charcoal and clear or brown amorphous weakly structured particles that are clearly vegetal matter. However, Patterson *et al.* (1987) suggested that it is the differentiation of the intergrade between the two groups where problems may arise. Waddington (1969) suggested counting only uniformly opaque particles to overcome this problem, and this technique was employed here. Particle size is thought to depend on the exact combustion process, the fuel type and on the dispersal mechanism and laboratory analysis procedures (Patterson *et al.*, 1987). However, there is some uncertainty associated with the difficult and time-consuming procedure of measuring the size of charcoal fragments and therefore this was not attempted.

4.3.2 Charcoal analysis

Despite these problems the role of natural and human-induced fire in ecosystem change is not in doubt. The fullest understanding of past environments cannot ignore fire and charcoal analysis of deposits would seem to offer perhaps the most comprehensive means of reconstructing fire events. Heinselman (1981) suggested that natural fires assist the spread of opportunistic, shade intolerant taxa, and Smith (1984) and Chambers and Price (1985) noted a coincidence of charcoal frequencies with the rational limit of *Alnus*, suggesting that the spread of this light-demanding species may

have been facilitated by the burning of closed forest.

There are numerous examples of high charcoal concentration associated with Mesolithic and Neolithic activity, such as in the studies of Innis (1981) and Simmons and Innis (1981) for the North York Moors. However, Patterson *et al.* (1987) draw attention to the fact that natural fires have also occurred throughout prehistory and that domestic fires from within dwellings or settlements will produce charcoal that could coincide with forest clearance phases, leading to the possibly erroneous inference of intentional burning of woodland. Clark *et al.* (1989) suggested that increased occurrence of fires in the absence of known human activity may reflect the palaeoclimate, *ie.* increased temperatures, decreased precipitation or increased availability of biomass. However, whatever the cause of fire, the use of complimentary techniques such as palynology, macrofossil analysis and charcoal analysis can greatly increase the understanding of processes and activities which have taken place in the past.

4.4 Macrofossil analysis

The interpretation of macrofossil records differs greatly from that of results of pollen-analytical investigations (Grosse-Braukmann, 1986), although it does serve as an alternative approach in the reconstruction of vegetation changes. Differences arise due to differing depositional and preservational processes of macrofossils as compared to pollen. The pollen content of peats and sediments primarily gives information on the vegetational character of the surroundings of the place of deposition; the macrofossil content, on the other hand, as a rule only gives information about the plant cover of the successional stages themselves, indicating the actual presence of a taxa at a site. Lake deposits may contain a macrofossil component brought to the site by flowing water, but it is thought that most macrofossils in the lacustrine environment are locally derived (Birks and Birks, 1980). Macrofossils can often be identified to species levels and this is important for taxa such as *Pinus*, where the pollen percentages required for local stands to be inferred are ambiguous, and other taxa, such as *Juncus*, which are not recorded in pollen diagrams (Watkins, 1991). However, as with most techniques, there are associated problems. Watkins (1991) suggested that macrofossils tend to be sporadic and rarely occur in significant numbers in core samples, making interpretations of changing frequencies difficult.

Most cores recovered for palynological studies are taken from the central areas of lakes and bogs which tend to contain little coarse organic material, whilst the optimum location for recovering macrofossils is towards the edge of a lake or peat bog as marginal deposits tend to be richer in plant remains (Seddon, 1962). Therefore a macrofossil study will require different site selection procedures to a palynological investigation. Peat bogs contain macrofossils of those plants actually growing over the bog although it must be remembered that a large proportion of the organic matter produced by the mire vegetation will have disappeared by decomposition (Grosse-Brauckmann, 1986), with preservation usually only occurring when above ground vegetative parts fall into more or less anaerobic environmental conditions such as water-filled hollows or luxuriantly growing moss carpets. Consequently, Grosse-Brauckmann (1986) has suggested that, with the exception of mosses, fruits and seeds, in general only the subterranean parts of mire plants form peat macrofossils. This also means that, as a rule, the subterranean organs of mire plants are growing within a peat matrix somewhat older than themselves, and it is possible for the peat-forming canopy to have a different origin to the peat layers, leading to the production of a mixed macrofossil composition. However, macrofossil analysis can provide a wealth of information as exemplified by studies carried out on Bolton Fell Moss and Walton Moss in Cumbria (Barber *et al.*, 1994). Such data from raised bogs have been used to reconstruct past climatic changes since these bogs derive all their moisture from the atmosphere and therefore it has been concluded that there is a relatively direct relationship between the mean water-table of a bog and effective precipitation (the balance of precipitation less evaporation).

Identifiable remains ($>118\mu\text{m}$) are recovered incidentally from pollen washings and can be analysed to obtain complimentary data on both the inorganic and organic content of cores. The results cannot form a macrofossil study in their own right, but for an input of relatively little extra time it is suggested that much additional information can be obtained (Watkins, 1991).

4.5 Loss-on-ignition (LOI)

It is widely believed that measurement of the ash content of a sediment sample may provide much valuable information on an environment and complement pollen analytical results (Aaby, 1986). In sandy soil landscapes, field erosion by wind is often reported at the present time, especially in spring when tilled fields lie bare and dust

particles can be transported over considerable distances. Similar incidents relating to past agricultural activity can be identified in mire deposits by an increase in the ash content of the peat.

The ash content of peat varies depending not only on the dust content of the atmosphere, but also on the ability of the surface vegetation to filter out particulate matter from the atmosphere, and on the rate of decay of peat and the degree of peat compaction. There will also be a "local" source of minerogenic material, namely biogenic opal such as diatoms, sponge spicules and phytoliths, although Vuorela (1983) suggested that in ombrotrophic *Sphagnum* peat the content of such material in ignition residues was too small to affect ash values.

Vuorela (1983) did, however, demonstrate the value of such a technique, especially when linked with pollen analytical evidence, such as *Cerealia* pollen. He suggested that LOI was a more useful indicator of the existence of arable land than selected pollen types due possibly to the small amounts of pollen liberated by species such as *Hordeum* and *Avena*. Walling (1994) proposed that analysis of the inorganic component of cores, or of the rate of sedimentation of inorganic sediment, is of value in the study of long-term patterns of sediment yield from a drainage basin. He suggested that the value of such studies also lies in the necessity for finding a baseline for soil erosion under undisturbed vegetation with which to compare present soil erosion rates. This technique was therefore used on samples from the cores extracted for pollen work.

4.6 Tephrochronology

The objective of this study was to test the hypothesis that volcanic ash, "tephra", is present in soils and sediments of North Wales. This involved a stratigraphic search for tephra followed by an analysis of its macroscopic, microscopic, and chemical properties. The presence of such layers in sediments of North Wales identifiable to specific volcanic events would provide a valuable time-synchronous marker horizon with which vegetational changes across a wide area could be dated and correlated.

4.6.1. Main source of tephra arriving in the U.K.

Kal-Y ash, supplied by A. Dugmore of Edinburgh University, has physical attributes characteristic of many deposits. Vitric shards range in size up to 200µm and are

isotropic. They have characteristic curved surfaces thought to be due to the formation of air bubbles, and are usually colourless. Material from any eruption can be characterised by such optical properties and by the geochemistry, especially in terms of the ratios of stable elements.

The main source area for tephra in the U.K. is Iceland. Baillie and Munro (1988) suggested that the violent eruptions of the Aegean island of Santorini in the second millennium BC could be detected, by reduced ring widths, in bog oaks of Northern Ireland, but thought that no detectable amount of ash was deposited over the British Isles at this time.

Iceland lies on the Mid-Atlantic Ridge, a volcanically active belt running from Jan Mayen in the Arctic across Iceland, the Azores and Tristan da Cunha, south to Bouvet Island in the Antarctic (Fridriksson, 1975), all these being peaks of a submarine mountain chain reaching up as high as 3000m, with deep valleys between. This fault line is termed a constructive fault since as the two plates pull apart, magma wells up, forming a ridge. Iceland straddles this fault along which lie volcanoes such as Hekla and Askja, as well as the recently formed island of Surtsey (Fridriksson, 1975). Such volcanoes are thought to have been active throughout the Quaternary period, for example the eruptions of Hekla in 1,120 \pm 50 BC (Hekla 3) and in 2,690 \pm 80 BC (Hekla 4) (Hammer *et al.*, 1980).

Tephra from such events has been found in peats and lacustrine sediments of Scandinavia and Scotland (Dugmore, 1991) and Northern Ireland (Pilcher and Hall, 1992), and there is therefore the possibility that it may be present in sediments of North Wales. Tephra, or pyroclasts in general, can be formed by any sub-aerial eruption, although the Surtseyan, Vesuvian and Plinian types of eruption are the most important in terms of high altitude pyroclastics (Francis, 1976). These eruptions are important in throwing material high into the atmosphere because of their characteristic combination of magma viscosity, gas content and water content (Decker and Decker, 1981), the later being able to turn a normally non-explosive basaltic eruption into a quite spectacular affair, as was the case of Surtsey, Iceland. Where this ejected material is finally deposited is dependent on a number of factors. Firstly, the smaller the particles the higher they will be able to go into the atmosphere, with particles of $<0.1\mu\text{m}$ shown to be able to stay in the upper atmosphere for more than one year (Mossop, 1964). Once the material is in the atmosphere its direction of travel will be dependent on the

direction of the wind (Harding, 1982).

4.6.2 Fate of airborne particulate matter

Much information concerning the deposition of ash has come from aircraft and satellite surveys (Tucker and Matson, 1985) and many of these studies concluded that small particulate matter would mainly be deposited by washout since it was being carried along in suspension (Erlandsson & Isaksson, 1988; Mattsson and Vesanen, 1988; Harvey and Wilson, 1988). Fiacco *et al.* (1993), in a study of the 1,479-1,480 A.D. Mount St. Helens eruption, found a sulphate peak in Greenland ice cores four months later than the eruption and subsequent ash deposition, suggesting primarily tropospheric transport of the ash and stratospheric transport of the sulphate aerosol.

Walker (1981) and Jakowsky (1986) suggested that material in the lower atmosphere is usually deposited very near the vent as a result of washing out whereas material which travels long distances is that which gets into the upper atmosphere and is moved by the upper wind systems. It is therefore theoretically possible for ash to be transported by jet streams and to eventually fall into the lower atmosphere, *ie.* to be transported over long distances by a combination of upper and lower atmospheric interaction as a result of the normal cellular circulation (Malloney and McVicker, 1993). There are many examples of the long distance transport of ash, including 9,000 BP Saksunarvatn (Iceland) ash found in northern Germany (Hunt and Hill, 1993) and the eruption of Mount Agung (Indonesia) in 1963, where dust was carried south as far as Sydney in Australia (Apsimon and Wilson, 1986).

There has been shown to be a good correlation between fallout and rainfall. Particles in the atmosphere act as hygroscopic nuclei in the formation of raindrops. This is important in the west of Britain, especially where rain (and dust) bearing winds from the NW are concerned. Along the west coast of Britain lie the main upland regions such as Snowdonia. As moist air is forced to rise over these ranges, it cools and so condenses, forming rain clouds and subsequently rain (Barry and Chorley, 1982). If the air masses had travelled across Scotland first, it is possible that any tephra may have been deposited over the highlands and so not be available to be deposited over Wales. Dugmore (1991) states the known minimum distribution of tephra from Holocene events to include Scandinavia and the Highlands of Scotland, and it has since been located in Northern Ireland as far south as the Mourne Mountains (Pilcher and Hall,

1992). As such it is possible that it will also be present in deposits from the uplands of North Wales, an area with abundant peat and lake sediments in which tephra deposits could have been preserved in a stratigraphic column.

4.6.3. Previous tephrochronological research

Tephrochronology has been applied to eruptions such as those of Mount St Helens (USA) and the Santorini eruptions (Mediterranean). However, the technique has only very recently been applied to Europe and the British Isles. Dugmore (1991) described tephra deposits in peats from Caithness (Scotland), detecting most of these layers by X-raying of peat cores to distinguish between peat and more X-ray dense deposits. These tephra falls, when mapped over a wide area (for example along an exposed peat cutting) often reveal the irregular nature of the surface that was masked by a single isochronous input of fine-grained material (Dugmore and Newton, 1992). Most of the work carried out on tephra shards has used electron microprobe analysis (Dugmore *et al.*, 1992; Blackford *et al.*, 1992), which is an essential analytical tool where both the volumes of material present and particle size are very small. Characteristic ratios of elements, such as Ti and Fe, have been used to correlate tephra deposits between sites and with tephra deposits from Iceland of known age. However, it has been shown that care is needed in such analyses, especially if based on the ferromagnesian minerals alone, due to the possibility of chemical weathering of such constituents with time (Hodder *et al.*, 1991), and so there is the need for the use of multiple criteria in these studies.

Tephra falls provide isochronous marker horizons which can be traced over long distances (>1000km). This is of considerable value since it can be used to guide the extraction of large quantities of peat of known relative age. This is of importance in studies of the radiocarbon content of different peat fractions or in the provision of material for inter-laboratory comparability exercises. Studies have also been carried out on the environmental impact such widespread dispersal of ash might have had. Blackford *et al.* (1992) showed a relatively rapid southward shift in the northern margin of *Pinus sylvestris* in Scotland around 4,000 BP. They suggested that this coincided with the deposition of Hekla 4 tephra and that this eruption caused, or contributed to, the death of trees growing in marginal locations some 900km from Hekla. Another example described by Baillie (1989) showed that some Irish bog oaks displayed a very spectacular narrow band of rings beginning in 1159 BC, which he related to the Hekla 3

eruption in Iceland. For a similar period in Scotland in the 12th century BC Burgess (1989) noted both the extensive abandonment of upland sites and a decline in the numbers of "burnt mounds", thought to relate to cooking at temporary hunting sites. These changes are suggested to have been brought about by the eruptions causing differing weather patterns, such that the increased stress on the marginal environments caused a decline in populations.

However, Grattan and Gilbertson (1994) suggested that volcanogenic climatic change is unlikely to have been the cause since they suggested that none of the Holocene eruptions of Hekla could have generated such a severe climatic change. They suggested that instead the environmental impact of volcanic aerosols may be the answer since this has been intimately linked to synoptic and local meteorology and environmental sensitivity of the ecosystems upon which they fell. Since palynological investigations seem to suggest that a strong regional bias in the severity of such impacts exists (Charman *et al.*, in press), they advanced the alternative hypothesis that acid loading caused by the deposition of acid volatile gases, either adsorbed on the surface of tephra grains or in aerosol form, emitted in Icelandic eruptions may have had direct but transient impacts on particular acid-sensitive ecosystems of Northern Britain and Iceland.

Certainly, the evidence from historical records (newspapers and diaries) seems to suggest extreme but localised impacts of volcanic aerosols released by the 1783 eruption of the Laki volcanic fissure in Iceland. This was noted across Britain and many European countries (Grattan and Pyatt, 1994; Grattan and Brayshay, in press). These events are therefore of much greater importance in the reconstruction of past environments than as just dating horizons.

4.6.4 Summary

Tephrochronology has the potential to provide much environmental information for an area of tephra deposition and may provide the solution to noted, but previously unexplained, changes in vegetation communities. The presence of tephra would also provide an isochronous dating horizon which would allow inter-site comparisons to be made without recourse to ¹⁴C dating.

4.7 Bioliths, including diatoms, phytoliths and sponge spicules.

Bioliths are mineral deposits laid down by organisms and include diatoms (algae), sponge spicules and phytoliths (produced in plant leaves, especially the grasses). Bioliths occur mainly in the silt/fine sand size range (Werner, 1977). Diatoms are the group which has been most extensively studied in terms of palaeoenvironmental reconstruction, as well as their present-day ecology.

Diatoms are of importance in palaeoenvironmental studies since they secrete a rigid cell wall, or "frustule", made up of amorphous hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$; Smithson, 1956), which will persist after the death of the organism (Bold and Wynne, 1985). Plant phytoliths are similar in that they are siliceous in nature, but are formed in the cellular tissues of some plant groups, such as the grasses (Smithson, 1956; 1958; 1959; Parry and Smithson, 1964). Being siliceous, it is widely believed that they are relatively resistant to decay, even in calcareous soils (Powers and Gilbertson, 1987), and as such they form, along with pollen, a valuable fossil record.

Although much work has been carried out into the ecology and palaeoenvironmental significance of diatoms less has been done concerning the significance of phytoliths and sponge spicules in soils and sediments as a record of past environments. Some of the lack of data in this field is possibly due to the techniques which have in the past been used to extract opaline silica from soils and sediments (Powers and Gilbertson, 1987), since the chemicals involved were costly, complex and unpleasant. Schuttler and Weaver (1986) described a technique of sieving and sedimentation to separate out the silt fraction after treatment with H_2O_2 to remove the organic matter. They then suggested further separation by a process described by Wilding and Drees (1971) and Yeck and Gray (1972) where the silt/fine sand fraction was repeatedly centrifuged in a heavy liquid nitrobenzene-bromoform mixture, a dangerous carcinogen, of specific gravity 2.3, to separate out biogenic opal containing the diatomaceous silica (specific gravity 2.00-2.07) from silicate minerals which have a specific gravity of >2.3 .

Powers and Gilbertson (1987) suggested an alternative method that involved only heating with acid, washing and then dehydration of the bioliths with methanol, with coarser grains being removed by the inversion the slide, since bioliths and finer particles will adhere to the glass and so remain whilst larger particles will fall off. Herbauts *et al.* (1994) suggested the use of zinc bromide (ZnBr_2 , $\text{sg}=1.92$) followed by determination

of alkali-soluble silicon in the extracted fraction by atomic absorption spectrometry. Some opaline silica particles have specific densities of up to 2.07, but the authors suggested that use of ZnBr_2 with a s.g. of 1.92gcm^{-3} is suitable since "previous investigations had shown that phytoliths always float under these conditions whereas soil particles sink". Battarbee (1986) concluded that the precise combination of steps must be determined experimentally in relation to the individual characteristics of the sediment being analysed.

The sediments used in this palaeoenvironmental reconstruction are mainly peat deposits, and so simply the removal of the organic matter, using the method given for tephra extraction, was found to be sufficient. A problem with any extraction is that diatoms may remain in colonies, so preventing single valves from being recognised and identified. This can be remedied by ultrasonic treatment which, although being effective, may also lead to the fracturing of some valves and so this treatment can only be used in a qualitative way as a guide to identification and relative frequency.

The record of diatoms in a sediment can be used to make inferences about past environments. It is suggested that assemblages of diatoms preserved in lake sediments can be directly related to the floristic composition and productivity of lake diatom communities, and as such can indirectly reflect lake water quality, especially pH, alkalinity, nutrient status and salinity (Battarbee, 1986; Davis, 1987). However, Battarbee (1986) points out that the preservation of the siliceous frustule can vary from site to site, identification can be difficult and palaeoecological interpretation must take into account the complexities of the sedimentary environment in which the frustules accumulated.

Diatoms have been recorded and classified for over two centuries. In the late Nineteenth century systematic and taxonomic investigations of modern and fossil diatoms began to be complemented by attention to aspects of distributional ecology (Cleve, 1894-95), but it was not until the second decade of the Twentieth century that the palaeoecological value of diatoms in lake sediments began to be recognised (Cleve-Euler, 1922). Since then, and with the help of the general floras developed by Schmidt (1874-1959) and Cleve-Euler (1951-55) diatomists have been able to address themselves to a wider range of palaeoenvironmental questions.

The use of diatoms in the reconstruction of past environmental conditions is often

combined with an analysis of the pollen fossil record (Pennington, 1943; Evans, 1970; Battarbee, 1978). However, diatoms do provide sufficient evidence concerning palaeoenvironments in their own right (Round, 1957; Haworth, 1976; Evans and Walker, 1977; Mannion, 1978; Flower and Battarbee, 1983; Battarbee, 1984).

Significantly fewer studies have attempted to use phytoliths or sponge spicules in palaeoenvironmental reconstruction. It is well known that phytoliths occur in Quaternary sediments in the British Isles (Dimbleby, 1967), and it has been shown that they can have great potential in environmental reconstructions (Grosse-Brauckmann, 1986). However, few studies have actually been carried out to tap this source, with the exception of work done by Armitage (1975), Macphail (1981) and Murphy (1986). Armitage (1975) described the value of phytolith studies in determining the diet of cattle from archaeological sites by extracting opal phytoliths from residual food material found on the cusps of their teeth. Such studies have concluded that although there are numerous problems relating to the use of bioliths in palaeobotanical studies, selected identification and grouping allows the differentiation of particular phytolith suites which not only permits the grouping and comparison of the Gramineae species present in each level, but also occasionally individual types may be recognised. Kurmann (1985) suggested that a combination of pollen and phytolith identifications is particularly valuable in the study of grasslands since phytoliths may be species- or group-specific whereas grass pollen is generally not.

4.7.1 Summary

As with palynological studies, analysis of bioliths can provide substantial supportive evidence in the recreation of past environmental conditions. This is particularly relevant where diatoms are concerned since there is a wide and good basis, including diatom taxonomy and previous studies, on which to base new work. This is not the case with phytoliths or sponge spicules, although analysis of the phytolith fraction in core samples can be a valuable technique in augmenting palynological work, especially concerning Gramineae species.

4.8 Radiocarbon dating

Radiometric dating is based on the disappearance or development of an isotope because of radioactive decay (Olsson, 1986). ^{14}C has now become a crucial part of

palaeoenvironmental work since it is no longer possible to accurately correlate sites using traditional pollen zones due to specific local site conditions. In order to do this it is now necessary to have a radiocarbon chronology. For the purposes of this project radiocarbon dates have been used to:

1. Date important vegetational changes within the local area;
2. Correlate and compare sites;
3. Calculate sedimentation rates;
4. Construct pollen concentration and accumulation rate diagrams;
5. Date specific features of ironpan stagnopodzols in an attempt to link soil development and vegetation change.

Dating is vital to the understanding of the development of this upland area in relation to N. Wales as a whole since few other dated vegetation sequences exist for Hiraethog. This is of special significance because of the level of human activity thought to have occurred here through the Mesolithic and Bronze Age as noted from the archaeological finds at Brenig and Aled Isaf (John Williams, pers. comm., 1994).

4.8.1 Theory

Terasmae (1984), Trumbore (1990) and Pilcher (1991) have recently summarised the theory of radiocarbon dating. Two techniques are used in this study - radiometric dating and accelerator mass spectrometry (AMS). AMS dating involves the counting of radiocarbon atoms directly in the sample rather than the disintegration events (Terasmae, 1984).

4.8.2 Potential problems

Before interpretations of ^{14}C dates are made, it is necessary to be aware of the associated limitations, problems, assumptions and errors. These are discussed below for samples from peat bogs and samples of charcoal and peat from soil profiles. The problems involved in the dating of mineral soil samples are more complex and are discussed in section 4.8.4.

4.8.2.1 Sample selection and contamination

During the sampling procedure using coring, sediment can become smeared down the sides of the core causing contamination, and thus prior to any analyses being carried out, including ^{14}C dating, the core surface needs to be cleaned of such material. Pilcher (1991) suggested that the greatest source of confusion in the interpretation of radiocarbon dates comes from poor sample selection, especially since many deposits are heterogeneous and are thus usually composed of a mixture of short-lived components such as mosses, remains of older components such as *Calluna* stems and the roots of plants that have penetrated from above, together with more mobile soluble materials. Samples from Cefn Mawr (see section 6.9), below 50cm, are beyond the root zone and thus contamination by roots is not likely to be significant; however, this may be a problem in the upper sections of the sediment core. Organic samples are usually treated with 2M HCl prior to dating to avoid contamination by more soluble organic components. Olsson (1986) described the problems associated with contaminants, especially those involving contaminants younger than the sample itself. For this reason modern rootlets, macrofossils and charcoal should be removed by hand, after sample surfaces had been cleaned to remove the effects of smearing.

4.8.2.2 Sample size

When sedimentation rates are slow it is possible for a thick sediment sample to represent an age span greater than the statistical error quoted for the radiocarbon measurement (Lowe, 1981), and so the smaller the sample size required the less the uncertainty. This is not so much of a problem with AMS dating of soil samples, but for the Cefn Mawr core, three 1cm slices were required to achieve the necessary quantity of organic carbon, and thus quoted dates are the average age of a 3 cm thick core section (see section 6.9).

4.8.2.3 Carbon isotope fractionation

There are three naturally-occurring isotopes of carbon, ^{12}C , ^{13}C and ^{14}C (Lowe and Walker, 1984), and although their general chemical behaviour is identical, they may react slightly differently because of their different masses (Olsson, 1986). This leads to isotope fractionation, the preferential enrichment of one carbon isotope compared to another, which occurs because of variations in temperature, pH and physiological

processes. It is proposed that there is good experimental and theoretical grounds for the general rule that any isotopic adjustment of the $^{14}\text{C}/^{12}\text{C}$ ratio is about double that of the $^{13}\text{C}/^{12}\text{C}$ ratio. The latter can be measured in the laboratory in a small sub-sample of the material to be dated and compared with a standard (PDB limestone) and therefore used for calibration (Lowe and Walker, 1984).

Damon *et al.* (1978) recommended that radiocarbon activities of all standards and samples be normalised to a standard $^{13}\text{C}/^{12}\text{C}$ ratio, or $\delta^{13}\text{C}$ value on the PDB scale: -25‰ for organic matter and -19‰ for the oxalic acid standard. This normalisation will compensate for environmental, biological and laboratory isotope fractionation. From a practical point of view, the corrections for fractionation are insignificant on a 30,000 year old sample because a correction of even 400 years is unlikely to be seen within the quoted plus or minus error for that sample. However, these corrections become increasingly significant for younger samples (Terasmae, 1984). A single peat sample, Olsson (1986) suggested, should be ascribed an uncertainty of ± 4 ‰ in the $\delta^{13}\text{C}$ value. An uncertainty of ± 5 ‰ on $\delta^{13}\text{C}$ is equivalent to ± 80 radiocarbon years.

4.8.2.4 Statistical uncertainties

Statistical uncertainty results from the nature of the radioactive decay, from the error in counting the decay rate of modern reference standards and fossil samples, and from the background noise (Chappell, 1978). Since radioactive decay obeys statistical laws it follows that the statistical uncertainty must be given. Olsson (1986) concluded that, unfortunately, there is no agreement between radiocarbon workers concerning the errors which should be incorporated in the stated uncertainty which arises from uncertainties in the $\delta^{13}\text{C}$ value, the size of the sample and the stability of the equipment.

4.8.2.5 Radiocarbon years and conventional calendar years

Variations in the $^{14}\text{C}/^{12}\text{C}$ ratio of carbon dioxide in the atmosphere are now well established from ^{14}C dating of samples of known ages, usually dendrochronologically dated material (Olsson, 1986). The result is a divergence between radiocarbon dates and calendar years and is thought to be due to variations in the ^{14}C production rate and/or climatically induced changes in the carbon cycle (Raisbeck *et al.*, 1994). It is suggested that the ^{14}C and dendrochronological scales converge at about 9,500 BP (Pilcher, 1991).

Ages determined from radiocarbon measurements using the half life of 5,568 years, normalised to $\delta^{13}\text{C} = -25\text{‰}$ and related to the international standard (supplied by the International Atomic Agency) are called "radiocarbon years" and are quoted in years "before present (BP)", "zero year" or present being AD1950 (Pilcher, 1991). These can be corrected for variations in the $^{14}\text{C}/^{12}\text{C}$ ratios and converted to calendar years, after application of one of the available age correlation curves or tables and are then termed "calibrated dates" (calBP; Olsson, 1986; Pilcher, 1991). Calibrated dates are of value in archaeological investigations for comparisons with historical records (Lynch, pers. comm., 1995). All dates in this study were calculated using the standard Libby half-life of 5568 ± 30 years for ^{14}C and are quoted both without calibration, and following calibration undertaken using a 20 year atmospheric model to 7,190 cal BC (circa 8,580 ^{14}C BP; Pearson and Stuiver; see Appendix VIc).

4.8.3 Construction of a depth-age profile

The calculation of the sediment accumulation rate is fundamental for the construction of a pollen influx diagram and this has to be based on a series of radiocarbon dates. It is generally believed (Berglund, 1986) that the integration of sedimentation rates, loss-on-ignition data and palynology can provide information on soil stability and changes in hydrological or climatic conditions. Sedimentation rates also allow the construction of pollen accumulation diagrams (Berglund and Ralska-Jasiewiczowa, 1986) and alleviate the inherent problem of sedimentation rate variability in concentration diagrams (Davis *et al.*, 1973).

Sediment accumulation rate curves are created by plotting radiocarbon dates against sample depth in a depth-age diagram. This can be performed in two ways; by joining the points for the mean age and the mean depth of each dated sample or by constructing a curve which fits to the dated levels. The first is thought to be the most accurate method when only a few dates are available (Berglund and Ralska-Jasiewiczowa, 1986), although with a greater density of dates irregularities in the constructed line may occur and the second method will give more reliable results.

All estimated or interpolated dates are taken directly from the depth-age diagram. The estimated time scale may be imprecise but is likely to be more accurate than dates extrapolated from other sites or from those based on assumption of synchronous vegetational events (Watkins, 1991).

4.8.4. ^{14}C and soils

The ironpan of stagnopodzols (placaquods), such as the Hiraethog series, is a critical feature, and one that is found in other upland regions of Britain, its presence probably relating to a distinct change in the soil regime. One very important question yet to be answered is the actual sequence of events leading to the development of these podzolic profiles. Was it (a) a case of the development of a thin iron-pan (placic Bf) horizon, leading to impedance and subsequent peat accumulation or (b) a case of a climatic change causing peat to accumulate, inducing water logging of an existing brown podzolic soil and movement of iron down the profile to produce the ironpan? The one date so far obtained for the iron-pan suggests the latter (as quoted in Avery, 1990) but further soil dates associated with the dated vegetation changes are essential to this basic question about the origins of one of our most widespread upland soils. The dating, therefore, of several iron-pans from this area should greatly increase our understanding of the processes, and the time-scales, involved in the development of the landscape of upland Britain.

Radiocarbon dating of soils has been plagued by numerous problems, many of which have yet to be solved. These include those already outlined in section 4.8.2, although problems of contamination are not so clear or easy to resolve. Scharpenseel (1971), in a review of the radiocarbon dating of soils, outlined the problems involved. He suggested that dating of wood charcoal and fossil organic horizons "beyond the root zone" was a standard procedure and account needed to be taken only of standard problems. He concluded that physical preparation of samples should always take place to ensure the removal of all fine roots, a point stressed by Ladyman and Harkness (1980), Harkness *et al.* (1986), Harkness and Harrison (1989) and Leavitt *et al.* (1994) in their suggested preparation procedures.

It is thought that there is an imbalance in the global carbon cycle, a "missing sink", and that soils may provide the answer. Trumbore (1992) concluded that an estimated 1,300 to 1,500 GtC ($1\text{GtC} = 10^{15}\text{gC}$) is stored globally as organic matter in the upper metre of mineral soils, roughly twice the estimated storage of carbon in the atmosphere, and consequently suggested there was a vital need to quantify the accumulation, transformation, translocation and eventual decomposition of soil organic matter on time scales ranging from seasonal to millennial.

Harkness *et al.* (1990) proposed that an opportunity to study the slow and rapid turnover rates of soil carbon was provided, inadvertently, by the nuclear weapons test programmes carried out during the late 1950's and early 1960's, which ejected a sharp pulse of ^{14}C directly into the earth's atmosphere. The subsequent and ongoing dispersal of this "bomb ^{14}C " excess by biogeochemical processes has provided unique conditions in which to trace and quantify mass transfer within the natural carbon cycle (Ladyman and Harkness, 1980; Harkness *et al.*, 1986; Harkness and Harrison, 1989; Trumbore, 1990; Harkness *et al.*, 1990; Trumbore, 1992). This situation means that the resolution of turnover times is no longer constrained by the slow rate of radioactive decay, but is limited by the steady decrease in atmospheric ^{14}C concentration as excess ^{14}C is transferred to the world's oceans. This has now allowed the creation of models to quantify carbon transport within natural soil systems and predict the likely long-term impact of management on the physical characteristics and nutrient status of forest and agricultural soils (Harkness *et al.*, 1990). It has also allowed a better understanding of N and P mineralisation rates. It is recognised by these workers that the ability to resolve these naturally induced variations will decrease progressively over the next several years as the man-made tracer tends towards a uniform distribution, although the availability of AMS, with its lower carbon requirements and faster processing, will alleviate some of this problem.

However, there are still significant problems in reliably dating soils, because of problems such as the continuous turnover of organic matter, bioturbation and mechanical mixing (Olsson, 1986). There is also a lack of understanding arising from the complex heterogeneous nature of soil organic matter (Stevenson and Elliot, 1990), which is made up of labile components as well as refractory components which may be stable for thousands of years (Trumbore, 1992).

Schappenseel (1971) had originally proposed that, with careful preparation, problems of this nature would not occur from samples isolated from, or not affected by, the carbon cycle, such as buried organic horizons and charcoal. However, he suggested that once buried organics become exposed due to erosion and once more become part of the root zone, rejuvenation of the humus occurs, although he gives no time scale for such a process. Geyh *et al.* (1983), from studies of buried sandy podzols, suggested that consideration must also be made of palaeorelief in the interpretation of ^{14}C soil dates, concluding that only in this way can autochthonous and allochthonous soil horizons and sediments be distinguished and the primary origin of the organic matter at the time of

soil formation be reliably recognised.

There are several differing suggestions concerning that fraction of the soil organic matter pool which is most suitable for dating. This obviously depends on the nature of the problem being investigated, although it is usually the most recalcitrant form that is required to give an idea of the oldest age of the soil, rather than simply a total mean residence time (MRT). One of the main problems is the lack of knowledge concerning the exact nature of soil organic matter, and the possibility that extractive techniques may well be producing artefacts rather than substances actually present in the soil. Leavitt *et al.* (1994) suggested that the process of physical removal of rootlets and hydrolysis with 6M HCl was sufficient to fractionate the soil organic carbon pool into relatively slow- and fast-cycling compartments.

It is thought that organic matter can become physically isolated in the clay and silt fraction, and thus separation of this could hold potential in the search for an "oldest" age of the organic fraction of soils. Scharpenseel (1971) proposed one such method of physical separation of a "clay-humus system", suggesting that this was the most stable carbon-bearing material and that it was much easier to clean of roots and tissue residues. He also suggested that the greatest ^{14}C ages were from 60-2 μm and 2-1 μm fractions, and that the <1 μm fraction gave a younger date due to the smallest particles being the youngest products of "crystallisation". Anderson and Paul (1984) and Skjemstad *et al.* (1993) also considered that over 35% of organic matter in clay and silt complexes could be protected from experimental photo-oxidation, which they thought mirrored the process which physically protects organic substances in soils against microbial degradation.

This is likely to have significance in attempts to date placic horizons, such as the B_f in ironpan stagnopodzols. There is evidence to suggest that the dating of at least the B_h horizons of sufficient depth and carbon content within podzolic profiles can be successful if the necessary precautions are taken (Cruickshank and Cruickshank, 1981), although there is little evidence in the literature concerning the dating of iron-pans themselves. This is because dating had only recently become a realistic option with the availability of AMS and its much smaller sample size requirements (2-5mg instead of 2-5gm for radiometric dating), as most iron-pans are generally thin and/or discontinuous and contain relatively small amounts of carbon. This had made it difficult in the past to get enough material for radiometric dating.

It is possible that a date from an iron-pan will be more accurate if organic matter within the pan has been trapped and protected by inorganic material and therefore rendered inert. Theng *et al.* (1992) provided evidence for the existence of recalcitrant long-chain aliphatic molecules being physically protected within the interlayer spaces of swelling clays (mica-beidellite structures). They found that isolation and dating of this material gave an older date than that for the soil as a whole and was therefore more likely to closely resemble the "true" age of the soil. Unfortunately, interlayer clay-humic complexes do not commonly occur in soil because their formation is conditional upon the soil having a smectitic clay mineralogy as well as a strongly acid reaction (Theng *et al.*, 1986). However, irrespective of clay type and pH, the organic matter in soil is largely associated with the mineral constituents through a variety of bonding mechanisms (Theng, 1979). An appreciable proportion is generally retained by clay-size particles which may aggregate into larger units which may create physical protection for humic substances (*ie.* by Fe/Al complexes). This fraction of humus is then considered to be stable against microbial decomposition and continuous soil cultivation (Tiessen and Stewart, 1983).

Thus, in the majority of cases, an inert organic matter fraction can be physically isolated from the soil matrix using conventional density and particle size separation methods (Oades *et al.*, 1987). However, chemical treatment of the isolate is sometimes necessary before the "true" radiocarbon age of the associated organic material can be assessed (Tsutsuki *et al.*, 1988; Theng *et al.*, 1989). In stagnopodzols, such as the Hiraethog series, a relatively pure placic horizon can obviously be physically isolated with relative ease from the rest of the soil so avoiding many contamination problems. It is, therefore, very likely that, within the iron-pan, organic material has been physically protected from decay, and that a date from this material may therefore give an indication of the time of iron-pan formation.

4.8.5 Summary

Radiocarbon dating is now an integral part of any palynological investigation, providing a chronology for comparable biostratigraphic events, although the advent of this procedure has obviously raised many questions which need further analysis. Its importance to this project arises from the necessity for chronological control and the need to correlate this data with that from other sites.

Radiocarbon dating of soil samples is a vital part of this, especially in terms of the rate of profile development and the podzolisation process. Since only one example of such a study is available (Avery, 1990), it will be of great interest to see how the results correlate, although at this stage in such a study it is possible that more questions will be raised than will be answered.

Chapter 5. Methodology

5.1 Introduction

This chapter will deal with the methodology used in this research project, both with the procedures chosen and also with the reasons for choosing these particular methods.

5.2 Physical and Chemical Analysis of the Soils

5.2.1 Introduction

Section 3.1. reviewed the literature concerning the chemical processes which are thought to have led to the development of the ironpan stagnopodzols and stagnogley soils found across much of the uplands of Britain. Many such theories, as well as soil classification systems, are based upon the analysis of physical and chemical characteristics of profiles, or at least of diagnostic horizons, and details of such results for these soils are presented by Ball (1960), Bower (1970), Rezk (1975) and Avery (1980; 1990). This information is used here to ensure that the soils studied are classified correctly, thus enabling direct comparisons to be made with other published work. This is also of value in the reconstruction of pedogenic processes which have occurred over time in these soils.

The range of soil properties which can be utilised is fairly extensive and the more used the more detailed the information and subsequent interpretations can be. The properties, and analysis of them, described here include those most commonly used for soils of this character (Avery, 1990).

5.2.2 Materials

Figure 2.6 shows the location of the ironpanstagnopodzol and brown podzol profiles. The two stagnohumic gley profiles were taken from exposures around Llyn Aled (figure 2.7). Profiles were chosen, during an initial visit to the site, which were visually representative of the soil series required. Profile locations are given below (as grid references).

Ironpan stagnopodzol

P1: SH91505960

P2: SH91405945

P3: SH91105928

Brown podzolic soil

P1: SH91055926

Stagnohumic gley soil

P1: SH92055760

P2: SH91825780

Unless otherwise stated, all physical and chemical analyses described below were carried out on air-dried sieved (<2mm) soil from each horizon of each soil profile. The field descriptions and locations of these profiles can be found in Appendix IV. The >2mm fraction was retained and weighed to give a % stone content.

5.2.3 Physical analysis**5.2.3.1 Soil Colour**

Colour has for a long time been recognised as one of the most obvious and more important profile characteristics used in the description and classification of soil diagnostic horizons (Avery, 1980; 1990). Bigham and Ciolkosz (1993) showed that soil colours are primarily related to their iron oxide, organic matter, moisture and salt (especially calcium carbonate) content. Colour has been used as a specific criterion in the identification of podzolic B horizons in relation to pyrophosphate extractable Fe and Al (Evans and Cameron, 1985), whilst soils darken with increasing humus content or with increasing humification of organic matter in peaty surface horizons (Birks and Birks, 1980). It is also generally accepted that the colour of soil darkens when moistened, and the apparent colour of wet soil is sometimes affected by reflection from surface moisture films (Hodgson, 1976). This has led to the development of soil colour (reflectance based) sensors which have been shown to be useful in determining many soil properties (Baumgardner *et al.*, 1985; Shonk and Gaultrey, 1989). Of importance in these soils is orange or red colouration, since it has been shown that these colour variations represent the form in which iron is present in the soil (Brown, 1953; McKeague and Day, 1966; Torrent *et al.*, 1983; Bigham *et al.*, 1991).

Munsell Colour Charts (1971) were used for the estimation of soil colour, on samples of field moist, air dried and ignited (550°C) soil, with field moist colours also being recorded for ped surfaces if different from the general horizon colour. Mottle colour and distribution was also recorded (Hodgson, 1976).

5.2.3.2 Particle Size Analysis

The grain-size distribution in a soil or sediment is an important physical attribute. It exerts a strong influence on such properties as porosity, permeability, shear strength, compaction and structure, as well as reflecting the history of the sediment, its mode of origin or parentage, and any subsequent modifications during pedogenesis (Kilmer and Alexander, 1949; Catt, 1985).

The first stage in the determination of grain-size distribution is the dispersion of the material into its constituent "prime particles". This provides a special problem with these soils since the parent material is predominantly silt- and mudstones, which with continued disaggregation will ultimately result in silt and clay only. Thus, here "prime particles" must be defined as silts, clays and silt and clay sized rock particles.

Most soils are bonded together with varying degrees of cohesion by clay minerals and organic colloidal material, or secondary minerals such as ferric and aluminium hydrous oxides or calcium carbonate (Deshpande *et al.*, 1964), and so different treatments of the soil will therefore produce different degrees of dispersion. The various methods most commonly used, either singly or in combination, include; boiling, mechanical stirring, ultrasonic dispersion and chemical treatment with sodium hexametaphosphate, HCl, sodium dithionite or hydrogen peroxide (Moshrefi, 1993). The main bonding agents in the soils studied were clays and iron and aluminium hydrous oxides. As such samples were chemically treated to deflocculate clays and then mechanically dispersed. In horizons containing high free iron and aluminium oxides analyses have been carried out on untreated samples and on samples after Fe/Al hydrous oxides had been removed by dithionite-citrate treatment.

In this study particle size analysis was carried out using the hydrometer and sieving techniques developed by Day (1965) as outlined in Sur and Kukal (1992). No particle size analysis was done on the peaty surface horizons since the properties of all fractions are dependent on the nature of the peat itself (Nordén *et al.*, 1992).

Selective removal of free iron oxides.

Samples of the B_{s2} horizon were treated overnight with dithionite-citrate to remove iron and aluminium. The samples, after subsequent washing with distilled water, were

then dispersed as outlined below. Samples were also run without prior removal of Fe and Al hydrous oxides.

Dispersion and fractionation of samples.

Hydrometer readings were taken after 40secs, 4mins, 37.5mins and 120mins, relating to the following size classes respectively; <50 μm , <20 μm , <6.3 μm and <2.0 μm . These hydrometer readings were corrected for the following;

1. Density of the dispersing agent ($\neq 1$); -2 units.
2. Temperature; 0.3 units added for each $^{\circ}\text{C}$ over 18 $^{\circ}\text{C}$.
3. Meniscus; the correction factor between the top and bottom of the meniscus on the hydrometer stem in clear water.
4. Hygroscopic moisture content; the moisture loss at 105 $^{\circ}\text{C}$ on a 5g sample of the soil over 24hrs was determined and used to calculate the dry weight of the original air-dried 50g sample.

Once the final reading had been taken, the soil was flushed gently through a series of nylon sieves to separate three more size fractions, 630 μm (25 mesh), 200 μm (72 mesh) and 63 μm (240 mesh). The washings were dried overnight at 105 $^{\circ}\text{C}$ and weighed. The results were converted to percentages and plotted as a cumulative frequency curve. Samples of the fine sand (63-200 μm) were retained for mineralogical analysis (section 5.2.3.3.).

5.2.3.3 Heavy Mineralogy

The heavy mineralogy of the 63-200 μm fraction of soils or sediments has long been used to supply information on the parentage and the processes that have acted on that material (Jenkins, 1964; Livesey, 1966; Younis, 1983; Bateman and Catt, 1985). Many workers have concluded that individual heavy minerals, or suites of minerals, are characteristic of specific lithologies, and this has been used extensively in areas such as North Wales to map soils and the glacial sediments from which they are derived (Smithson, 1953; Livesey, 1966).

The dominant rock types making up the Hiraethog uplands are Silurian siltstones and mudstones which have a characteristic suite of minerals including chlorite (dominant), tourmaline, zircon, magnetite and rutile (Livesey, 1966). Some extraneous minerals have been recorded, such as kyanite and amphiboles, although these are not thought to

relate to material deposited by Irish Sea or Welsh ice respectively, but are thought to be of aeolian origin (Livesey, 1966).

Samples used were the 63-200 μm fractions obtained from the particle size analysis. Heavy minerals were separated by the use of a suitable liquid with a specific gravity of 2.95 gcm^{-3} . The method adopted was that developed by Jenkins (1964) as outlined in Younis (1983) where the sample was repeatedly dispersed in tetrabromoethane (s.g. 2.95) in a tapered centrifuge tube and centrifuged. The two fractions were separated by the careful introduction of a suitable plunger to seal off the heavy fraction.

The two fractions obtained were examined microscopically immersed in methyl salicylate (R.I. 1.54), and also as a permanent mount in Canada Balsam. Grains were identified as far as possible by their optical properties using transmitted light with a standard petrological microscope.

5.2.3.4 Fabric Analysis of Parent Materials

An analysis of the preferred orientation of the long axis of stones and erratics in sediments, *i.e.* fabric, has also been used to determine the origin of materials (Holmes, 1941; Fernlund, 1993). It is a useful technique in the differentiation of glacial drift and periglacial head deposits, the latter being oriented in the direction of the slope. This is especially useful in an area such as Hiraethog due to the uniformity of the bedrock source sediments and the susceptibility of the siltstones to weathering which leaves little other evidence, such as striations, to show ice flow directions.

The field techniques used here are as described in Saunders (1968). The subsequent diagrams drawn up to illustrate the results were (i) a rose diagram, showing the independent analysis of the preferred long axis orientation in 10° classes, (ii) the direction and amount of the long axis plotted on a polar equal-area graticule so that each pebble is represented by a dot whose location indicates both the direction and the angle of plunge.

5.2.4 Chemical analysis

5.2.4.1 Hydrogen Ion Activity (pH)

The pH of soils is not an independent variable, but rather a function of several interrelated factors such as the composition of parent material, the rate of leaching and biological activity (Beniamino *et al.*, 1991). However, pH is a valuable parameter since from it inferences can be made concerning many other soil properties, such as Al³⁺ solubility (Reuss *et al.*, 1990), Fe, Mn, Zn solubility (Neite, 1989) and weathering of silicate minerals (Frank and Gabhardt, 1990).

The method used is that given by Avery and Bascomb (1982), using both H₂O and 0.01M CaCl₂ in a ratio of 1 part soil to 2.5 parts liquid. The values presented are the means of duplicates.

5.2.4.2 Organic Carbon

The analysis of organic carbon is of particular importance in these soils. Organic matter contributes to soil fertility and cation exchange capacity (Thompson *et al.*, 1989) and so maintenance of soil organic matter content has implications in terms of soil management and land use. In the soils of the Hiraethog Moors, typically ironpan stagnopodzols, the amount of organic matter and organic carbon are thought to be related to the podzolisation process. Gorshkova and Lyapina (1990) showed that when a podzolic soil was flooded and organic matter introduced, there was a considerable increase in amorphous (oxalate extractable) iron, the greatest increase being noted in the B horizon. Herman and Gerke (1992) also show the ability of humic substances to complex with iron(III) and aluminium in humic podzols, and this process is thought to be of importance in the formation of podzolic features (Rezk, 1975; Lundström, 1993).

Loss-on-ignition has been widely dismissed as a crude and inadequate estimate of organic matter or organic carbon content in soils (Jackson, 1958) on the grounds that, in addition to the main weight losses from the destruction of organic matter, further weight loss occurs due to loss of CO₂ from carbonates in calcareous soils, to loss of elemental C and to loss of structural water from clay minerals. However, the soils under study are non-calcareous, and Ball (1964) found loss-on-ignition was a reliable method for organic matter estimation for soils, and at 375°C errors due to structural water

losses were minimised. Davies (1974) concluded that the presence of calcium carbonate in soils does not affect its loss-on-ignition value at 430°C, although a problem may be posed by those soils having gibbsite and goethite in their clay fraction, for it is reported in the literature that both minerals dehydrate at around 300–400°C (Hsu, 1989; Schwertmann and Taylor, 1989).

Tinsley's (1950) modification of the chromic acid digestion procedure of Walkley-Black (1934) was used in the estimation of organic carbon. Samples were digested with dichromate and then titrated against ammonium ferrous sulphate using phenyl anthranillic acid as an indicator.

Charcoal fragments, hand-picked from the B_{s2} horizon of the ironpan stagnopodzol, were collected. Some fragments were made into thin sections as detailed in section 5.4, whilst others were identified under the stereozoom microscope by Dr P. Denne of the School of Agricultural and Forest Sciences, University of Wales, Bangor.

5.2.4.3 Cation Exchange Capacity (C.E.C.), Exchangeable Ca, Na, Mg and K and Base Saturation (%)

The total quantity of negative charges per unit weight of a soil, that is its "cation exchange capacity" (C.E.C.), is an important aspect of its chemical behaviour, as is the composition of the loosely held, or "exchangeable", cations which balance this charge. The C.E.C. has no absolute value, varying with the particular cations involved, their concentrations and the pH, but its estimation under specified conditions provides results of value for comparing the nutritional status of soils (Wild, 1988). The method used for this analysis is one commonly adopted by other workers (eg. Ngewoh *et al.*, 1989; Manrique *et al.*, 1990). However, it must be remembered that this analysis is carried out at pH 7.0 whilst the soils under study are generally below pH 5.0.

Exchangeable cations were displaced by NH₄⁺ and the quantity of Ca⁺⁺, Na⁺ and K⁺ measured by flame emission photometry, the effect of interference in the case of Ca²⁺ being suppressed by dilution of the standards and samples 1:1 with 5000µg/ml La³⁺ solution. Mg⁺⁺ was determined by atomic adsorption spectrophotometry. C.E.C. was determined by displacing NH₄⁺ with 1M KCl and estimating NH₃ by distillation with caustic soda, trapping the NH₃ in boric acid and indicator and titrating against 0.025M H₂SO₄.

Base saturation is the ratio, expressed as a percentage, of the exchangeable metallic cations and the C.E.C..

5.2.4.4 Extractable Fe, Al and C from <2mm fractions

Aluminium, iron, silicon and organic carbon have long been used as parameters in the characterisation of podzolic soils (eg. McKeague and Day, 1966), and three extractants, dithionite, oxalate and pyrophosphate are commonly used in the differentiation of these materials. Iron oxides can be differentiated by other methods, such as XRDA, but Younis (1983) outlined several difficulties which can occur with this (i) The iron oxides usually constitute a small percentage of temperate soils (ii) The iron oxide peaks are broad (*ie.* poorly crystalline and small particle size) and they are difficult to recognise when peaks due to other mineral components are also present (iii) In the presence of goethite the strongest haematite peak (0.269 nm) overlaps with the (130) peak of goethite.

For the purposes of this study the following processes were employed, thereby also allowing quantification of Fe in its different forms.

1. Dithionite-citrate: considered to dissolve all forms of iron occurring in soils (Mehr and Jackson, 1960; Livesey, 1964). [Fe_d]
2. Oxalate: extracts poorly crystallised (amorphous) forms of iron oxides (Schwertmann, 1973; Farmer *et al.*, 1983). [Fe_o]
3. Pyrophosphate: extracts largely that fraction of iron in the form of organic complexes (McKeague *et al.*, 1971). [Fe_p , Al_p , C_p .]

Dithionite-citrate extractable Fe (Fe_d)

This was carried out using the procedure outlined in Livesey (1964) who showed that this method removed more iron from soils than the dithionite-citrate-bicarbonate method proposed by Jackson (1958) and Mehr and Jackson (1960). The extracted iron was measured colourimetrically with thiocyanate using a spectrophotometer. Selected samples were also estimated by atomic adsorption spectrophotometry, using an air/acetylene flame, to check the accuracy of the above method.

Oxalate Extractable Iron (Fe_o)

This extraction was carried out using the standard procedure outlined in Schwertmann (1973) and Phillips and Lovley (1987). The iron in the extract was estimated by atomic adsorption spectrophotometry, (PYE Unicam SP9-10), using an air/acetylene flame.

Pyrophosphate extractable Fe, Al and C (Fe_p , Al_p , C_p)

Extraction was carried out using the procedure outlined in Avery and Bascomb (1982). Fe and organic C were determined as above. Al was determined colourimetrically as outlined in Avery and Bascombe (1982).

5.2.4.5 Extractable Si, Fe and Al from $<2\mu\text{m}$ fractions

Clay samples ($<2\mu\text{m}$) for each horizon were also analysed by NaOH and dithionite-citrate for amorphous iron, silicon and aluminium since amorphous materials are thought to occur extensively in these soils (Dudas and Harward, 1971; Arshad *et al.*, 1972). Amorphous ("without crystalline form") minerals do not have the regular 3D packing arrangements found in crystals although there is no sharp dividing line between crystalline and amorphous materials (Wada, 1989). They are assumed to be the result of weathering of primary and secondary minerals, and since they are in many instances associated with the surface of clays and humus colloids, the physical, mineralogical and chemical properties of soils will be disproportionately influenced by these materials (Sawhney, 1958; McKeague *et al.*, 1971; Johnson and Yeh, 1974)

The amorphous materials which are of importance in soils are oxides and hydroxides of Al, Fe and Si, and silicates of Al and Fe, all in various states of hydration (Wada, 1989). Since the soils under investigation are highly acidic ($<\text{pH } 5.0$) it is likely that the weathering products of chlorite form amorphous aluminosilicate (Kodama and Brydon, 1968; Coen and Arnold, 1972), particularly in the surface horizons which often contain very little chlorite.

The use of strong inorganic acids, followed by NaOH solution to dissolve the released SiO_2 , has traditionally been employed to dissolve the non-quartz fraction of soil (Jackson, 1956) and alkaline reagents have been used to dissolve amorphous aluminosilicate, free silica and free aluminium. For example, boiling clays with a dilute Na_2CO_3

solution is a widely accepted practice to facilitate complete dispersion of clay particles by dissolution of amorphous cementing materials (Jackson, 1956).

Being highly insoluble in alkali, iron acts as a protective barrier limiting accessibility, and as a consequence, the solubility of silica and aluminium. However, use of a citrate chelating agent with dithionite for free iron oxide removal dissolves some silica and aluminium and makes accessible for alkali dissolution silica and aluminium cements that are stabilised by iron oxide coatings (Follet *et al.*, 1965). In fact, Henderson and Duff (1963) who studied the solubility of silica from natural silicate minerals and soils found that silica was brought into solution by citric acid produced by several species of microbe (*e.g. Pseudomonas*). Hashimoto and Jackson (1960) proposed a single treatment of boiling with 0.5N NaOH for 2.5 minutes which has been shown to dissolve out similar quantities of amorphous materials (Farmer *et al.*, 1983). Poorly crystalline hydrous oxides are characteristic of weathered podzolic horizons and in particular of andic horizons containing allophane derived from the weathering of glass in volcanic ash falls. The presence of such material can also be detected by the pH rise resulting from the displacement of loosely held OH⁻ by F⁻ ions (Johnson and McBride, 1989).

NaOH Extraction.

The method outlined by Hashimoto and Jackson (1960) was used whereby clay samples were boiled with 0.5M NaOH for 2.5 minutes in nickel beakers. The dissolved Si and Al were determined immediately, Si by the method outlined in Pruden and King (1969) and Al by the method outlined in Dougan and Wilson (1974). The residue was then extracted with citrate-dithionite and the supernatant analysed for Fe as outlined in section 5.2.4.4.

Dithionite-citrate extraction

The extraction method of Livesey (1964) was adopted, in which sodium dithionite in citrate buffer was shaken with clay samples (1g) for 16 hours. Fe was estimated as above. Al estimation was as outlined above, except that before the analysis it was necessary to destroy the citrate because it interferes in the colourimetric determination of Al (Rezk, 1975). This was done by digesting a suitable aliquot (5ml) with a 3:1 mixture of HNO₃ and H₂SO₄ in a porcelain crucible, first by gentle heating on a low temperature hot-plate to dryness (past fuming) and then in a muffle furnace at 450°C

for 4 hours. When cool, the residue was taken up in 1N HCl (5ml) on a low temperature hot-plate for 15 minutes. When cool the contents were transferred quantitatively to the polythene bottles.

Si was determined by the procedure outlined in Rezk (1975) to overcome the interference from dithionite, iron and phosphorus.

5.2.4.6 NaF test

This was carried out by the method outlined by Johnson and McBride (1989) where saturated NaF solution (pH7.0) was added to representative samples. The pH of the dispersed sample was measured after 1 hour of intermittent stirring with the pH meter carefully calibrated at pH 7.0 and 9.0. Values of pH >10 are indicative of significant amounts of amorphous materials.

5.3 Clay mineralogy

5.3.1 Sample Preparation

Air-dried sieved soil (<2mm) was used, the main steps involved being a) sedimentation ± the removal of cementing agents b) Mg²⁺ and K⁺ saturation c) preparation of orientated samples d) ethylene glycol treatment of Mg²⁺ saturated samples e) heating to 550°C of K⁺ saturated samples f) treatment with dimethyl sulphoxide (DMSO).

5.3.1.1 Removal of cementing agents

Pretreatment to remove cementing agents and amorphous materials "is thought to be of value" in cleaning clays to give clearer diffraction patterns (Hashimoto and Jackson, 1960; Mehra and Jackson, 1960), but indiscriminative use of such methods can also lead to the loss of much valuable information or the production of artefacts (Mehr and Jackson, 1960). Organic matter, calcium carbonate, iron and amorphous materials are most commonly removed, although in this study it was decided to run samples initially with no pretreatment and also to run samples with all amorphous materials removed. Iron was removed with dithionite-citrate (Livesey, 1964) from B_s horizons of the stagnopodzol, as well as from the E_{ag} horizon of the stagnogley to determine what effect, if any, the process had on clay minerals.

There is considerable variability in the kinds of pretreatments which can be used for cleaning clays of amorphous materials, although it is usual that at least two extractants are used (Farmer *et al.*, 1983). The dithionite-citrate system (Livesey, 1964) was chosen since citrate is well known for dissolving silica (Henderson and Duff, 1963), whilst boiling for 2.5 minutes with 0.5N NaOH, described by Hashimoto and Jackson (1960) was employed for its capacity to dissolve allophane and free alumina and silica. The method described by Farmer *et al.* (1983) using oxalate and pyrophosphate extractants to remove the allophane-imogolite complex was not employed since they also showed that boiling with 0.5N NaOH removed similar quantities of Si and Al.

Clay residues, after extraction with NaOH to remove Si and Al and then citrate-dithionite to remove Fe, were treated in the same way as outlined below and then analysed by X-ray diffraction. The methodology for these extractions is described in section 5.2.4.5.

5.3.2 Separation of the clay fractions

The process of sedimentation is that which was developed to study particle size distributions (Day, 1965; Bouyoucos, 1953 & 1962; Sur and Kukal, 1992), as outlined in section 5.2.3.2., except that after dispersion with the plunger the material was allowed to stand undisturbed for 8 hours, at 20°C, before the top 10cm of liquid was siphoned off (or 16 hours and 20cm); this represents the clay fraction (Kilmer and Alexander, 1949). This process was repeated up to 5 times in order to obtain sufficient clay material.

5.3.3 Subdivision of the <2µm fraction

Analysis of the various size fractions of clay rather than the bulk sample can be of value in the detection of small quantities of minerals concentrated in a certain size fraction that may be masked by the more abundant minerals. Three subfractions were obtained, 2-0.63µm, 0.63-0.2µm and <0.2µm, but due to time constraints it was decided to analyse the bulk sample and the <0.2µm samples; if these showed significant differences then the remaining size fractions would be analysed.

The subdivision was carried out by sedimentation under centrifugal force; the time required for the sedimentation of particles of particular diameter and specific gravity

being calculated using the integrated form of Stokes equation as calculated by Shahid (1988).

5.3.4 Mg²⁺ and K⁺ Saturation

Saturation was carried out as described by Shahid (1988). 50mg of clay sediment was redispersed in distilled water and the clay pipetted onto a slide and allowed to dry at room temperature, giving rise to the orientated samples as described below. Samples from each horizon were prepared as orientated samples without this treatment and run over the range 2-50° 2 Θ to check for other minerals present with spacings below 0.7nm.

5.3.5 Preparation of orientated samples

Sedimented aggregates consisting of clay suspensions dried onto a flat surface, such as a glass slide, were used successfully since they lead to preferred orientation of the clay particles as they settle, as well as allowing smaller particles to settle out last and so lie at the surface where they will be preferentially scanned. This preferred orientation of the sheet-like clay particles enhances the d(001) diffraction maxima, thus resolving the diagnostic c, or more precisely the c sin β , dimensions of the various clay minerals (Shahid, 1988).

5.3.6 Instrument

XRD analysis of all slides was carried out using Mn-filtered Fek α radiation generated by a Phillips PW1140 at 50kV and 40mA. Diffraction patterns were detected by a wide range goniometer (PW1050) with a 1°/0.1mm/1° slit system, scanning at 1°2 Θ /min and recorded on a chart at 1cm/1°2 Θ with a time constant of 2 seconds and a c.p.s. rate of 1x10⁴ or 4x10³ over a range of 2-18° 2 Θ for clays and 2-50° 2 Θ for rock and untreated samples. Traces for each successive treatment of a sample were offset.

5.3.7 Sample Treatments

5.3.7.1 Ethylene glycol test

Treatment of the Mg²⁺ saturated samples with ethylene glycol vapour is a diagnostic

test for distinguishing between the swelling and the non-swelling clay minerals, and for studying mixed layer clays (Moore and Reynolds, 1989). The prepared and scanned Mg^{2+} saturated slides were subjected to ethylene glycol vapours at $60^{\circ}C$ for two hours and then rescanned between $2-10^{\circ} 2\Theta$ within one hour of the slides being removed from the vapour to prevent the evaporation of the ethylene glycol and the collapse of clay minerals which had swelled.

5.3.7.2 Heat treatment

Heating of samples in a muffle furnace to $300^{\circ}C$ and $500^{\circ}C$ can cause the collapse of certain minerals. The scanned K^{+} saturated slides were used for this purpose. Kaolinite can be detected from heat treatment, although other minerals, such as chlorite, change in similar ways, and so a more protracted method, using dimethyl sulphoxide, was required as described below.

5.7.3 Kaolinite test

The procedure developed by Lim *et al.* (1981) as outlined in Shahid (1988) was used. This swells the first order peak of kaolinite (0.71nm), which normally overlaps the second order peak of chlorite, to 1.12nm. Slides were run immediately on drying to prevent the collapse of any swelled kaolinite. Samples of a kaolinite standard were also run to check the procedure.

5.3.8 Preparation of parent material samples

Samples of parent material were collected, washed and dried. Sections were cut, ground and polished, as described in section 5.4.2.2, parallel and perpendicular to the cleavage to produce a flat and smooth surface. Samples were then run as described over the range $2-50^{\circ} 2\Theta$.

5.3.9 Criteria for the identification of clay minerals

"The basis of the analytical procedure for clay minerals by X-ray diffraction is that the diffraction pattern of each crystal is determined by its atomic spacings which assign a unique sequence of diffraction maxima, so that the pattern serves the purpose of identification" (Shahid, 1988). The identification of clay and other minerals is often

complicated when there is a wide range present, such that peaks overlap so that some minerals become hidden. As such, the tests outlined above are designed to allow identification by showing differing properties of individual minerals. The differentiating criteria and analysis of many such minerals are given by Conway (1980), Brindley and Brown (1980), Shahid (1988) and Moore and Reynolds (1989) from which the following table of principle basal spacings (nm) after various treatments has been developed for the main clay minerals found in these soil samples.

Table 5.1 Principle basal spacings of selected clay minerals.

	Principle basal spacings ¹				
	Untreated	Mg ⁺⁺	Mg ⁺⁺ /Glyc.	K ⁺	K ⁺ /5-600°C
Kaolinite ²	0.71-0.72	0.7	0.7	0.7	-
Hydrous mica	1.00-1.02	1.0	1.0	1.0	1.0
Chlorite ³	1.41-1.42	1.4	1.4	1.4	1.4
Vermiculite	1.40-1.50	1.4	1.4	1.0	1.0
Verm/mica					
Reg. interstrat.	2.4	2.4	2.4	1.0	1.0
Irreg. interstrat ⁴	1.2	1.2	1.2	1.2	1.2

NB

- 1. There is often a small variation about the values quoted for the different varieties of each mineral.**
- 2. Specific test for kaolinite with DMSO shifts peak to 1.12nm.**
- 3. Some chlorites (poorly crystalline; "secondary") may collapse to 1.0nm on heating to 300-500°C.**
- 4. The values of basal spacings of irregularly interstratified clay minerals will vary according to the proportions of the two components.**

5.4 Micromorphology

5.4.1 Sampling

5.4.1.1 Selection of sampling sites

The profiles already chosen for general soil analysis and clay mineralogy were also sampled for this micromorphological study. This obviously incorporates a certain degree of preselection, and a more extensive study should involve random selection of sites. This is augmented by the fact that each horizon identified in the field was sampled, thus again involving preselection, although this factor was reduced by the sampling of horizons and boundary zones and of taking samples from upper and lower B_s horizons. However, in future studies each randomly chosen profile should be sampled at regular intervals to avoid this problem altogether. Samples were also collected from certain other features which were thought to be of interest. Profile locations and field descriptions are given in Appendix IV. Samples of charcoal were removed from profile 3 of the ironpan stagnopodzol and prepared as thin sections as detailed below to facilitate the identification of charcoal in soil thin sections.

5.4.1.2 Sample collection

The soil materials collected need to be undisturbed in order that their internal patterns and organisation remain intact. The simplest method of achieving this was to use specially prepared Kubiena tins (83x90x123 mm), which had a single hinged corner and removable end pieces. For soft, friable material these were simply pushed into the exposed soil section, removed carefully, excess soil material trimmed off and then sealed with the end pieces and bound with masking tape, ensuring sample orientation was clearly marked. Sample compression was minimised by cutting around the edge of the tin as it was being pushed into the soil. For some samples tins were not required (and were not feasible) due to the hardness and/or stoniness of the material. In these cases blocks were removed carefully and placed in plastic bags, again with the orientation clearly labelled.

5.4.1 Thin section manufacture

5.4.2.1 Sample impregnation

The impregnation of undisturbed soil blocks was carried out using a polyester resin which is immiscible with water. Consequently, it was necessary to remove moisture from the samples prior to impregnation. This was done by placing the undisturbed soil blocks into glass or aluminium foil-lined polythene containers after carefully removing them from the tins and leaving them to air-dry until no further weight-loss was recorded. At the same time, markers were placed in each container showing the depth and horizon the sample came from. There are, however, problems with shrinkage of organic rich materials with air-drying, and thus the approach outlined by Fitzpatrick and Gudmundsson (1978) was adopted where water in the peat was replaced by acetone by exposing the wet block to acetone vapour of increasing concentration up to 100%. The block was then impregnated with resin immediately to avoid shrinkage resulting from vapourisation of the acetone. This, or alternative procedures such as freeze-drying, were not employed generally for soil blocks due to the cost and the relative ease of air-drying, and the problems of disturbance due to ice-crystal formation in the case of freeze-drying.

The resin (unsaturated polyester resin in styrene monomer) was mixed with acetone in a 50:50 mixture to facilitate the penetration of the resin into the soil blocks. A hardener, methyl ethyl ketone peroxide, was also added at a level of 1.5% of the total mixture. This was then left to cure at room temperature in a fume cupboard until hard (4-6 weeks). Often the top few millimetres did not harden properly and the blocks were therefore placed in an oven at 40°C for a further 24 hours.

5.4.2.2 Slide preparation

Once blocks were sufficiently hard they were knocked out of their containers (glass containers needed to be broken off) and cut up depending on the needs of the study using a diamond saw (Logitech CS10), with a suitable lubricant (Abralap). The blocks were cut to give vertically and horizontally orientated slices.

Once suitable slices had been cut, they were ground on one side using a rotating diamond plate, and then hand-ground and finally polished, using 6µm and 1µm Hyprez

diamond pastes with a Kent MR2 Lapping Machine, to ensure that the face of the soil block that would be adhered to the glass slide was absolutely flat. Logitech glass slides, 47x27mm and 76x110mm, were chosen that had as little variation in thickness as possible to ensure the production of a uniform specimen. Soil blocks were stuck to slides using a 2 part Epoxy Resin (Type 301, Logitech) in a ratio of 4:1 by weight. This was slowly placed on the prepared face of the block, ensuring that all air spaces had been filled. With very porous materials a vacuum was used prior to the adherence of the slide. The blocks were placed in a vacuum desiccator with resin evenly spread over their surface. The desiccator was evacuated, using a moderate vacuum, until bubbles appeared in the resin. This ensured that the pores were filled with resin and air bubbles would not form once the slide was placed on the surface. The block was then placed on the glass slide and held in a logitech clamp for 24hours until set.

The impregnated slices, once cleaned of any excess resin, were sawn off using the diamond saw and associated vacuum chuck to leave about 1mm of soil block on the slide. This was then ground down further using a rotating diamond plate, and then down to 50 μ m thickness using a Logitec jig system (PM2a Precision Lapping and Polishing Machine). The final grinding, to 30 μ m, was carried out by hand using a 5 μ m grinding powder (with Abralap lubricant) on a perspex sheet. When the sections had been ground to the required thickness they were polished on the lapping machine, using paraffin as a lubricant, with 6 μ m, 1 μ m and 0.5 μ m Hyprez diamond pastes. The slide was then clearly labelled.

After each stage the blocks and/or slides were ultrasonically cleaned in ether to remove any loose soil or grinding powder. The removal of the latter is especially important if the sections are to be subsequently used for EDXRA. A full description of the stages of thin section manufacture can be found in Fitzpatrick (1984). Both large (76x110mm) and small (27x47mm) slides were made for each horizon to give both vertically and horizontally orientated slices.

5.4.3 Routine Thin Section Description and Analysis

The descriptive system used is that outlined in Bullock *et al.* (1985), and involved the description of each thin section in terms of 5 categories as follows:

1. Microstructure
2. Basic mineral components

3. Basic organic components
4. Groundmass
5. Pedofeatures

However, there are additional problems in the description and identification of organic matter in soil thin sections, and so additional terms defined by De Coninck *et al.* (1988) were also used and are noted as such. Fitzpatrick (1988) gives a descriptive summary of roots, both live and dead, as seen in thin sections which was also made use of.

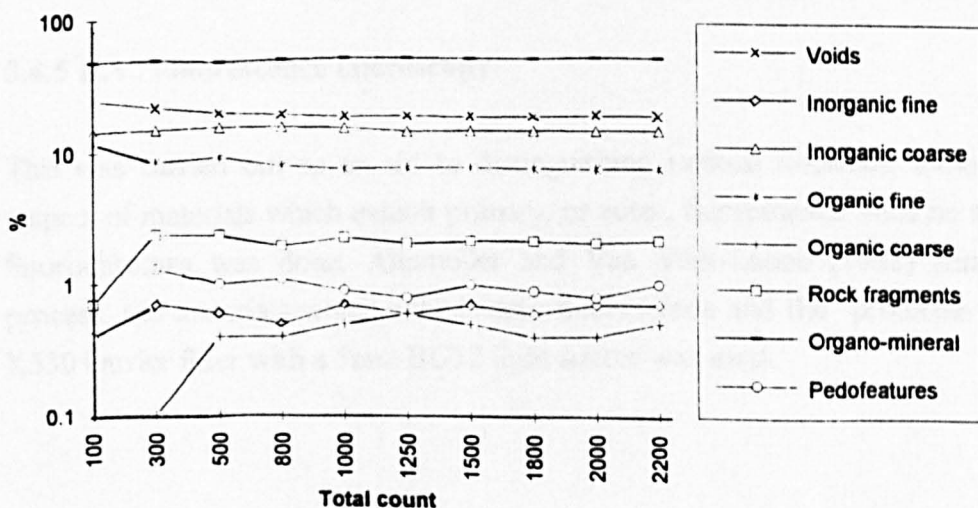
In order to achieve an accurate analysis of the distribution of features throughout the profiles, point count analyses were carried out, with up to 2000 points/slide being counted, with the following categories included:

1. Voids (>30 μm)
2. Coarse inorganics (>10 μm)
3. Fine inorganics (<10 μm)
4. Coarse organics (>5 cells connected in original tissue)
5. Fine organics (<5 cells)
6. Pedofeatures

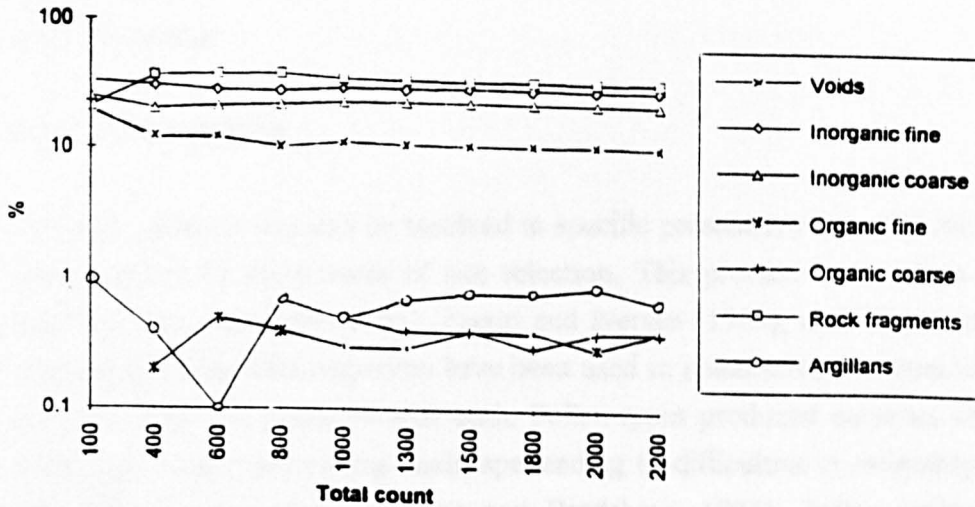
A figure of 2000 was chosen since after this little variation in percentages occurred. This was determined by recording percentages for the above categories throughout a point count, as graphically represented below (see Appendix I for data).

Figure 5.1 Changes in the frequency for selected micromorphological features with increasing point count total.

Stagnopodzol E_{ag}



Stagnopodzol BC



5.4.4 Energy dispersive X-ray analysis

Jenkins (1970) summaries this technique, the equipment needed and the value of such an approach in micromorphological studies. Bisdom *et al.* (1981) updated this, describing some of the new software now available. This technique has been used to analyse the B_s fabric, in particular the pale-yellow material, the B_f in terms of the relative distribution of Al, Fe, Si and Mn and the composition (Si,Al,K,Mg) of different phases of clay deposition. Selected areas in sections were initially extensively photographed with the light microscope, at magnifications x4 to x40, and then selected areas were cut out to leave around 1cm² which were then mounted on SEM stubs. These were coated with C for an initial study. All SEM/EDXRA work was carried out on the Hitachi S520 Scanning Electron Microscope, using 14kV and 150μA emission current, connected to a Link Analytical QX2000 system with a Multiwindow LZ4 detector. After analysis, samples were coated in gold, using a SEM coating unit E5000 Polaron Equipment Ltd, to facilitate photography of the relevant features.

5.4.5 U.V. Fluorescence microscopy

This was carried out as an aid to distinguishing various materials, although only in respect of materials which exhibit primary, or auto-, fluorescence since no staining with fluorochromes was done. Altemoller and Van Vliet-Lanoë (1988) summarise this process, the materials which exhibit auto-fluorescence and the problems involved. A K530 barrier filter with a 5mm BG12 light source was used.

5.5 Environmental analyses

5.5.1 Materials

5.5.1.1 Site selection

The level of detail that can be resolved in specific palaeoenvironmental reconstructions is determined by the process of site selection. This process is described in detail by Jacobson and Bradshaw (1981), Faegri and Iversen (1989), and Moore *et al.* (1991). Peat deposits and lake sediments have been used in palaeoenvironmental investigations although there are problems with both. Pollen types produced on peats are often also produced on the surrounding landscape leading to difficulties in estimating the size of the pollen source area (Jacobson and Bradshaw, 1981). Pollen grains of aquatic angiosperms will also be found in lake sediments, but for the most part are morphologically distinct from pollen produced on peats and therefore do not pose such a problem. The most useful method of studying local pollen changes is thought to be to use paired sites so that data from peat and lake sediments can be correlated to give a more accurate picture (Donner *et al.*, 1978). Jacobson and Bradshaw (1981) suggested that all types of lake may have potential for palynological studies, but that small, well-protected lakes would have less internal variability and would be less susceptible to pollen-stratigraphic changes that have resulted from past shifts in prevailing winds.

Moore *et al.* (1991) suggested that the following points should be taken into consideration when deciding on the suitability of sites for palynological investigations:

1. **Depth of sediment:** a more complete stratigraphic sequence most frequently relates to the deepest sediment. Also, deepest sediment will relate to a greater accumulation rate so allowing a higher degree of resolution.
2. **Avoidance of local pollen influences :** many sites have peripheral regions (lagg) in which tree species such as *Betula*, and *Salix* grow which should be avoided.
3. **Avoidance of areas where sediment disturbance is suspected,** for example lake margins and areas of peat cutting or erosion.

5.5.1.2 Selected sites for palynological study on the Hiraethog Moors

Two possible sites were located from maps and field visits. The first, a peat bog (Cefn Mawr, SH908573), seemed to meet all the criteria for a palynological investigation. It is a slight basin about 10m below the surrounding landscape, 200m in diameter. It is drained from the NE end and an outcrop of steeply dipping (15-20°N) sandstone was present at the SW edge. The bog was probed along two transects (NE-SW and NW-SE) with steel rods to study the depth of peat present. The deepest peat was found near the centre of the bog with a depth of 430cm. From the probing it seemed as if the underlying surface had once consisted of a series of ponds/channels (Chapter 6).

The second possible site was a small natural lake, Llyn y Foel-frech (SH919594), about 100m in diameter. Present-day lake morphometry was deduced using a Raytheon Depth Sounder from an inflatable boat. After calibration of the instrument, sufficient transverses were completed, with positions being fixed using parallel aligned poles, to allow the production of a depth contour map. At its deepest point Llyn y Foel-frech contained 4.5m of water (figure 6.25), accurate to within ± 25 cm due to the transitional boundary between seston and water not producing a well defined reflection (Watkins, 1991). This water depth suggested the lake would be suitable for further analysis.

5.5.2 Coring procedures

Initial cores from the deepest part of Cefn Mawr were taken using an Eijkelkamp gouge corer, but subsequent cores were extracted using a Russian corer (for descriptions of all coring equipment see Moore *et al.*, 1991). On recovery, cores were placed into split plastic drainpipes, wrapped in cling film and aluminium foil and labelled. Duplicate overlapping cores were taken to make certain that a complete sequence was recovered and to provide back-up material for additional pollen analysis and radiocarbon dating.

Llyn y Foel-frech was cored using a Livingstone piston corer (chamber size 100x5cm) from a raft secured over the deepest part of the lake following the procedure outlined in Watkins (1991). Core depths are given from the top of the seston although the transitional seston was too liquid to be collected. These core sections were treated as described above for the peat. All cores were stored at 4°C to prevent desiccation and microbial activity. In all stages of coring care was taken to minimise the risk of contamination, although the possibility of material falling into core holes when coring

cannot be totally ruled out.

5.5.2.1 Materials/core descriptions

Core descriptions are given in Appendix VI. In the laboratory core sections were opened and cleaned by running a spatula across the surface parallel to the stratigraphy to prevent vertical contamination. Cores were described using the Troels-Smith sediment descriptive system as outlined in Birks and Birks (1980). In this, sediment was described in terms of its physical properties (colour, stratification), its humification (the degree of decomposition of organic material) and its composition.

5.5.3 Pollen analysis

5.5.3.1 Core sampling

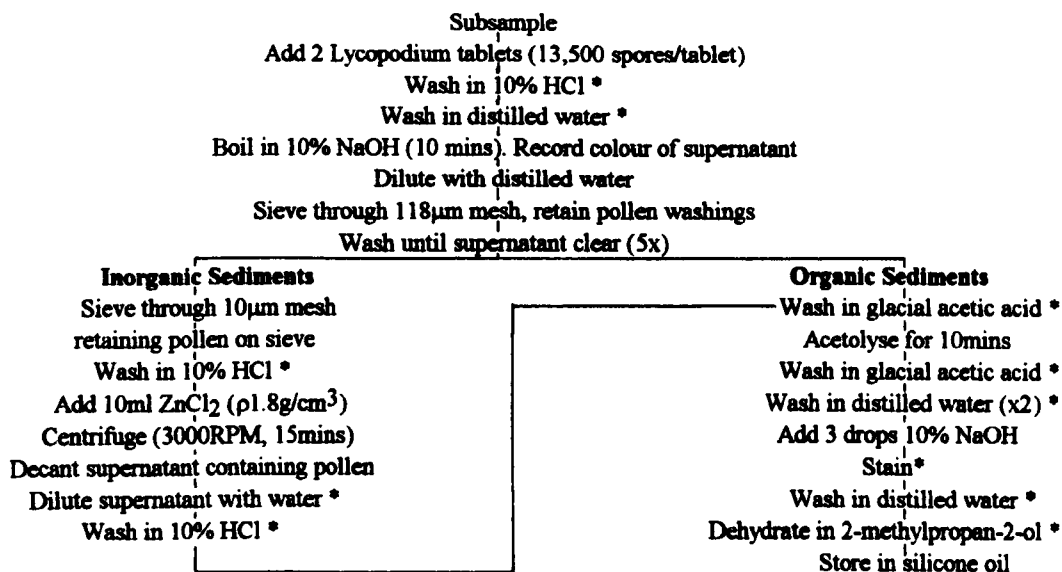
After cleaning the surface of cores to reduce the risk of contamination, samples were taken using a cylindrical volumetric sampler of 0.5cc. This was pushed into the material, removed, excess sediment cleaned off and the 0.5cc of material extruded into a test-tube. For organic-rich sediment only 0.5cc was required, but because of lower pollen concentrations in the minerogenic material more was required, usually 2-5cc. This was done by weighing 0.5cc of material, removing a section across the core at the relevant point, weighing this and calculating the corresponding volume of material. Cores were sampled at regular intervals such that intermediate samples could be taken at a later date to increase the resolution of the resulting pollen diagram as required.

5.5.3.2 Pollen extraction

This was carried out using the procedure outlined in Berglund (1986) and Moore *et al.* (1991). A schematic representation of this procedure is given below, taken from Watkins (1991), who outlines the reasons for the use of $ZnCl_2$ as compared to HF.

NB. 1 For inorganic sediments it was sometimes necessary to repeat the sieving at $10\mu m$ after acetolysis to produce a cleaner sample.

NB. 2 * = centrifuge (Gallenkamp Labspin)



5.5.3.3 Pollen identification and counting

Slides were prepared by spreading a small volume of homogeneous residue, with extra silicone oil if required, evenly over a clean glass slide and sealing it with a slide cover glass held in place with nail varnish at each corner (Watkins, 1991). Using the keys of Faegri and Iversen (1989) and Moore *et al.* (1991), and the reference collection at the University of Wales, Bangor, pollen grains and spores were identified to the lowest possible taxonomic level.

For judging the accuracy of a pollen spectrum Berglund and Ralska-Jasiewiczowa (1986) recommend that unidentified grains are also classified. This information has a bearing on the depositional conditions, in lacustrine as well as terrestrial environments (Lowe, 1982; Tipping, 1987). Cushing (1967) and Birks and Birks (1980) suggested that unidentified pollen grains may be classified as follows (definitions of terms are outlined in Berglund and Ralska-Jasiewiczowa, 1986)

Unknown:

Indeterminable:	{	<p>Corroded</p> <p>Degraded</p> <p>Broken</p> <p>Crumpled</p> <p>Concealed</p>
-----------------	---	--

Grains that had been affected by more than one of the above were ascribed to the dominant type (Tipping, 1987).

Counting was carried out using a Leitz microscope. A magnification of x400 was used except for critical identifications when oil immersion and a magnification of x1000 was used. To avoid the problem of differential pollen dispersion on the slide due to different grain sizes, traverses were regularly spaced and covered the whole slide (Moore *et al.*, 1991).

5.5.3.4 Calculation of Results

The following calculations and definitions, taken from Berglund and Ralska-Jasiewiczowa (1986) unless otherwise stated, have been used.

1. The pollen sum

Birks and Birks (1980) suggested that to reduce statistical errors in the calculation of pollen spectra it was necessary to count grains until each pollen type is a constant percentage of the pollen sum; a total of 500 for tree taxa being considered adequate to reflect forested landscapes with general vegetational changes. Moore *et al.* (1991), however, suggest that for minor components (below 5% representation) a count of >1000 grains is preferable.

A pollen sum (P) of 300, including trees, shrubs and herbs but excluding spores and aquatics was used, and other categories (spores, aquatics, indeterminables and unknowns) were recorded separately; this allowed a greater number of samples to be counted in the time available. For organic samples, counts of over 300 appropriate grains were obtainable from one slide, but this was not possible for minerogenic samples where low pollen concentrations rendered this target unattainable and counts varied between 3 and 305 over one or two slides. These have still been included in the pollen diagrams since they can provide useful information when plotted in concentration diagrams.

2. Pollen percentages

Tree, shrub and herb species pollen are calculated as a percentage of the total land pollen (tree, shrub and herb pollen). Spores, aquatics and indeterminables are calculated as a percentage using the total land pollen plus that particular group; this avoids the

problem of having any taxa greater than 100%.

ie.

Pollen sum (P) = sum of [trees + shrubs + herbs]

Spores (S) % calculated as a percentage of [P+S]

Aquatics (AQ) % calculated as a percentage of [P+AQ]

Inderterminables (ID) % calculated as a percentage of [P+ID]

3. Pollen concentration (Pconc)

The number of grains per unit volume of wet sediment (g/cm^3)

$$Pconc = \frac{\text{exotic spores added} \times \text{fossil pollen counted}}{\text{spores counted} \times \text{volume}}$$

(See Moore et al. (1991) for details of exotic spores which can be added).

4. Sediment accumulation rate (SAR)

The net thickness of sediment accumulated per unit time after compaction and diagenesis. This is estimated from a series of radiocarbon dates and measured in cm/yr.

5. Pollen accumulation rate/influx (PAR)

The net number of grains accumulated per unit area of sediment surface per unit time. Units are grains/cm²/year (gr/cm²/yr).

$$PAR = Pconc \times SAR$$

$$\text{or } = Pconc / \text{deposition time}$$

5.5.3.5 Pollen diagram construction

Percentage, concentration and accumulation data have been plotted against depth, and diagrams were constructed using the TILIA program (Designed and produced by E. Grimm of Illinois State Museum, Springfield, Illinois). A time scale is included, based on radiocarbon dates supplied by NERC Radiocarbon Laboratory (NERC Allocation 520/1292), as well as local pollen assemblage zones (LPAZ), coded and numbered from the base up. Graphic output as a continuous curve as opposed to a histogram makes overall trends easier assess but also does involve data interpolation (Moore *et al.*, 1991).

5.5.4 Charcoal analysis

The method used is that described by Patterson et al. (1987) as used by Watkins (1991). Six evenly spaced transects across each slide, previously prepared for pollen counting, were traversed and all charcoal fragments and exotic marker grains within the field of view were counted. Charcoal concentrations were calculated using the formula:

$$\text{Charcoal concentration} = \frac{\text{Exotic grains added} \times \text{charcoal counted}}{\text{Exotic grains counted} \times \text{sample volume}}$$

This data was plotted against depth and incorporated into TILIA to allow direct comparison with the pollen analytical data presented.

5.5.5 Plant macrofossils

Macrofossil analysis was limited to the small sediment residue collected on the 118 μ m mesh during standard pollen preparation procedures. This material was studied under a x10-x50 binocular microscope and components divided into three main categories; recognisable remains, unidentifiable organics and the inorganic fraction (Watkins, 1991). The latter two groups were subdivided into a fine and coarse component, the division between fine and coarse minerogenic material being the division between medium and coarse sand (\approx 0.6mm; Hodgson, 1976). Abundances of unidentifiable components were recorded on a four point scale (Watkins, 1991). Identification of the sparse recognisable remains was undertaken using photographs (Godwin, 1975) and drawings (Burrows, 1974). However, due to lack of reference materials this was restricted to a few taxa. Results are presented in Appendix VI.

5.5.6 Loss-on-ignition

1 cm³ samples were removed from cores at 2.5cm intervals. These were placed in crucibles, dried at 105°C, weighed and then ignited at 450°C in a muffle furnace for 24 hours and reweighed when cool. Percentages of organic and inorganic matter were calculated as percentages of the dry (105°C) weight. Material was retained for possible future chemical analyses.

5.5.7 Tephrochronology

The presence/absence of tephra was investigated at two sites. The first involved the use of a core from a lowland lake on the Arfon Platform, Llyn Cororion, (collected by R. Watkins) since it had an associated set of radiocarbon dates (Watkins, 1991). The second involved the use of material collected from Cefn Mawr once it had been ^{14}C dated. This allowed the possible location of tephra falls from known Icelandic eruptions to be found. Two eruptions of the Hekla volcano were chosen, Hekla 3 (3070 \pm 50 BP) and Hekla 4 (4640 \pm 80 BP)(Hammer *et al.*, 1980).

These points in the cores were located, and then a section extending 30cm either side of this point were also removed to take into account errors in ^{14}C dating and variability in sedimentation rates. This 60cm of core was divided into three 20cm sections and X-rayed using a cabinet x-ray system (Faxitron Series) with an exposure time of about 2 minutes.

Where X-ray dense material was highlighted on the X-radiographs the extraction procedure outlined in Lascelles (1993) was carried out. Samples were mounted in Canada Balsam and a study made of their optical properties. Some material was also prepared for SEM/EDXRA to be photographed and to allow analysis of the geochemistry, especially in terms of Fe/SiO₂ ratios. However, Pilcher and Hall (1992) have noted that igniting to 600°C can increase the K⁺ content of tephra samples and therefore suggested the use of Dugmore's (1989) wet oxidation method if material is to be analysed by EDXRA.

5.5.8 Opaline silica analysis

Organic samples were treated in the way outlined for tephra. Opaline silica was separated from minerogenic sediments by the method outlined in Yeck and Gray (1972). Samples were prepared for both light microscope and SEM/EDXRA studies.

5.5.7 Radiocarbon dating

5.5.7.1 Sampling of peat material

Slices 1 cm thick were removed from the core (5cm diameter semi-circle) at points

previously chosen to give as much information as possible *ie.* from points of abrupt and important vegetation change noted in the pollen diagram for Cefn Mawr. Slices 1 cm thick were also removed either side of the middle point and all samples sent to the Radiocarbon Dating Laboratory (NERC-RCL) in East Kilbride to ensure enough material had been supplied. Samples were dried and subjected to standard preparation and counting techniques at the NERC-RCL.

5.5.7.2 Soil samples

Two of the stagnopodzolic profiles previously studied (P2/P3) were used for this study. AMS ^{14}C dating was employed here due to the small quantities of carbon present within ironpans. This was carried out with the assistance of a NERC grant (GR9/1518) to cover beam-time hire at the AMS dating facility in Arizona.

Samples of ironpan were physically removed from soil profiles and stored wrapped in aluminium foil in polybags. From P2 samples of charcoal from below the pan and samples of peat from the base of the overlying O_h were also removed and stored as above to allow the ironpan dates to be bracketed. These latter two samples were refluxed with 2M HCl to remove contaminants at the NERC-RCL. They were then combusted to CO_2 and sent to the AMS dating facility in Arizona.

With the exception of dates obtained by Scharpenseel, as quoted in Avery (1990), no work has been done on dating of ironpan horizons from such soils. It was therefore decided to fractionate the carbon present and date the residue left, as well as a bulk sample, in an attempt to find the oldest age of this feature. Initially, samples were washed in distilled water to remove as much as possible of the overlying root mat and underlying B_s horizon. Samples were then air dried and, using a binocular microscope, remaining excess materials were scraped off using a mounting needle. Special care was taken to ensure all rootlets and underlying B_s had been removed. These were then washed of dust, dried and ground to a fine powder.

Previous experiments on similarly treated material had been carried out to analyse total carbon content (C_T) and extractable carbon by various methods (C_p , C_d and C_{HCl}). Carbon in both the extractant and the residue was determined. For obvious reasons, dithionite extraction was carried out without the use of citrate buffer. All experimental procedures are outlined in section 5.2.4.3.

From the results it would appear as if dithionite was extracting a similar amount of carbon as HCl, and so it was decided to date bulk samples and the residues after pyrophosphate and HCl extractions. Extractable C fractions were not dated since these are expected to give younger ages and these can be calculated from the difference between the ages of the residue and bulk samples. All material to be dated was combusted to CO₂ and sent to the AMS dating facility in Arizona.

Figure 5.2 Chemical analysis of ironpan samples from the Hiraethog series (ironpan stagnopodzol). Scale bar = 0-9%

Organic carbon

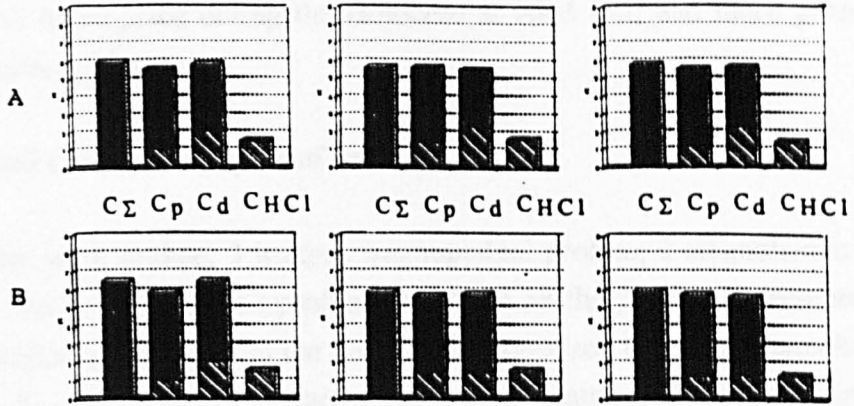
C_{Σ} = total organic C

C_p = pyrophosphate extractable C

C_d = dithionite extractable C

CHCl = HCl extractable C

(Hatched areas represent organic C remaining in the residue after extraction by named chemical)

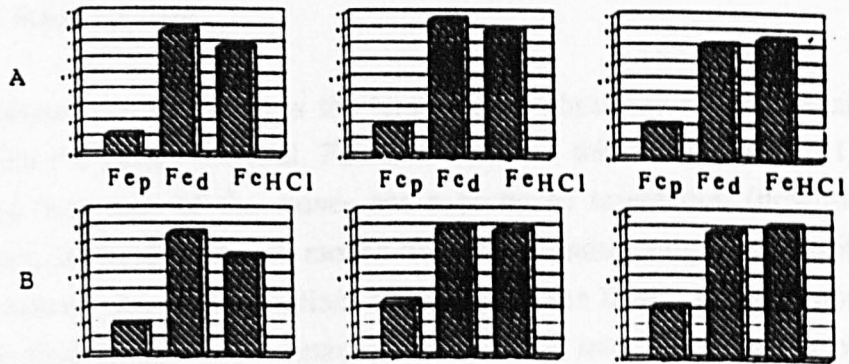


Iron

Fe_p = pyrophosphate extractable Fe

Fe_d = dithionite extractable Fe

FeHCl - HCl extractable Fe

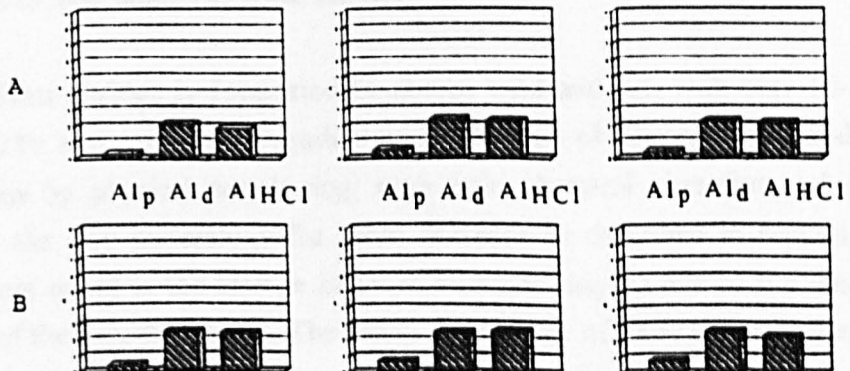


Aluminium

Al_p = pyrophosphate extractable Al

Al_d = dithionite extractable Al

AlHCl - HCl extractable Al



Chapter 6. Results and Discussion

6.1 Introduction

This chapter aims to present the experimental data obtained during this research project and to discuss the results in terms of the soil and environmental changes which may have taken place during the Holocene at Aled Isaf, and more generally across the Hiraethog Moors.

6.2 Physical and chemical analyses of soils

Five soil profiles were studied, 3 ironpan stagnopodzol profiles, 2 staghomic gley profiles and 1 brown podzolic soil profile. Data from all the profiles is presented in Appendix II, whilst data from P3 of the ironpan stagnopodzol, P1 of the staghomic gley soil and P1 of the brown podzolic soil are presented and discussed in the following text. Differences between profiles of the same soil series are highlighted where they occur.

6.2.1 Ironpan Stagnopodzol

The lowest horizon sampled (BC) is the least altered physically and chemically in comparison with the parent material. Fabric analysis on this material (fig 6.1) has shown that the long axis of the stones has a preferred orientation (downslope), suggesting that it is "head" material, moved downslope under periglacial conditions. Figure 6.1, however, shows two distinct directions of the fabric, and this possibly represents the divergence of the material due to the undulating nature of the underlying solid geology, exposed in places around the margins of Aled Isaf by wave erosion. Stones (>2mm) make up over 50% of this lowest horizon (fig 6.2) and are angular in shape, reflecting the fact that much of the "head" material would probably have originated as frost shattered rock deposits.

The texture of this horizon is dominated by coarse sand and silt, with only 10-12% clay (fig 6.2). This again represents gradual disaggregation of the parent material into smaller particles by physical weathering, with little chemical alteration, which is highlighted by the clay mineralogy for these horizons as described in section 6.3. Slight differences noted in the texture of these horizons may be due to the inherent heterogeneity of the parent material. The heavy mineralogy of these lower horizons is

dominated by chlorite, with some tourmaline and zircon, a suite of minerals characteristic of Silurian silt- and mudstones (Appendix IIb).

Figure 6.1 Fabric analysis of the parent material of an ironpan stagnopodzol (a) rose diagram showing the preferred long axis in 10° classes (b) the direction and angle of plunge of the long axis, each dot representing one stone. Slope direction is WSW.

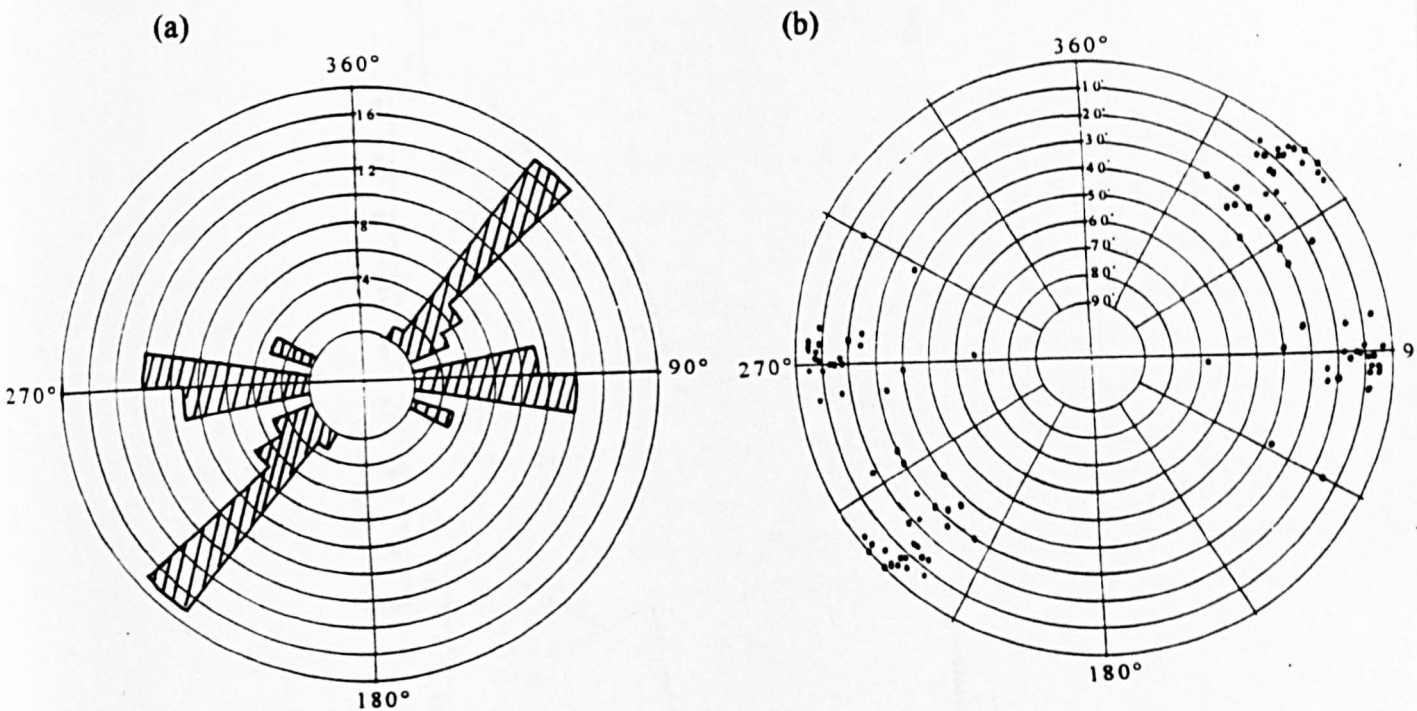


Figure 6.2 Summary of particle size analysis of an ironpan stagnopodzol (P3) including % stone (>2mm) content.

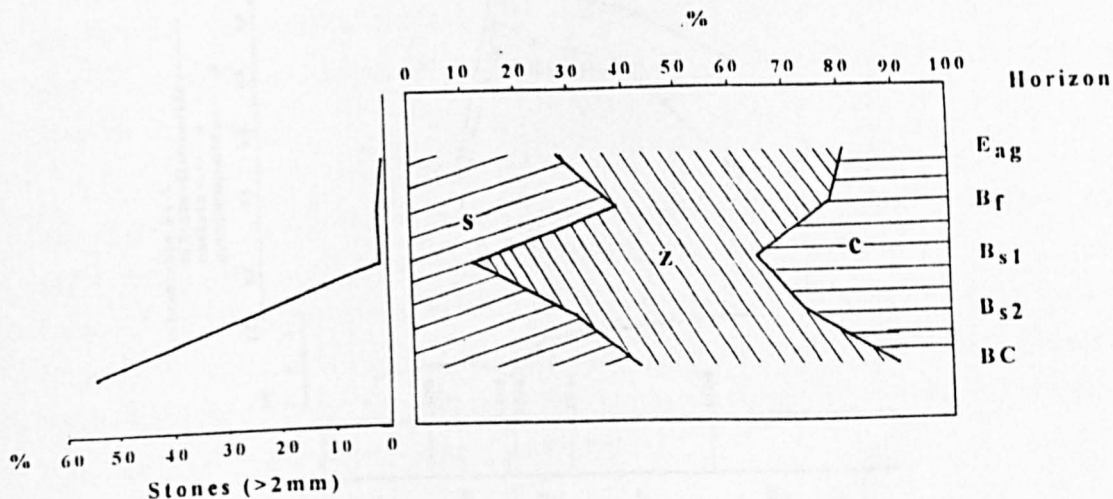
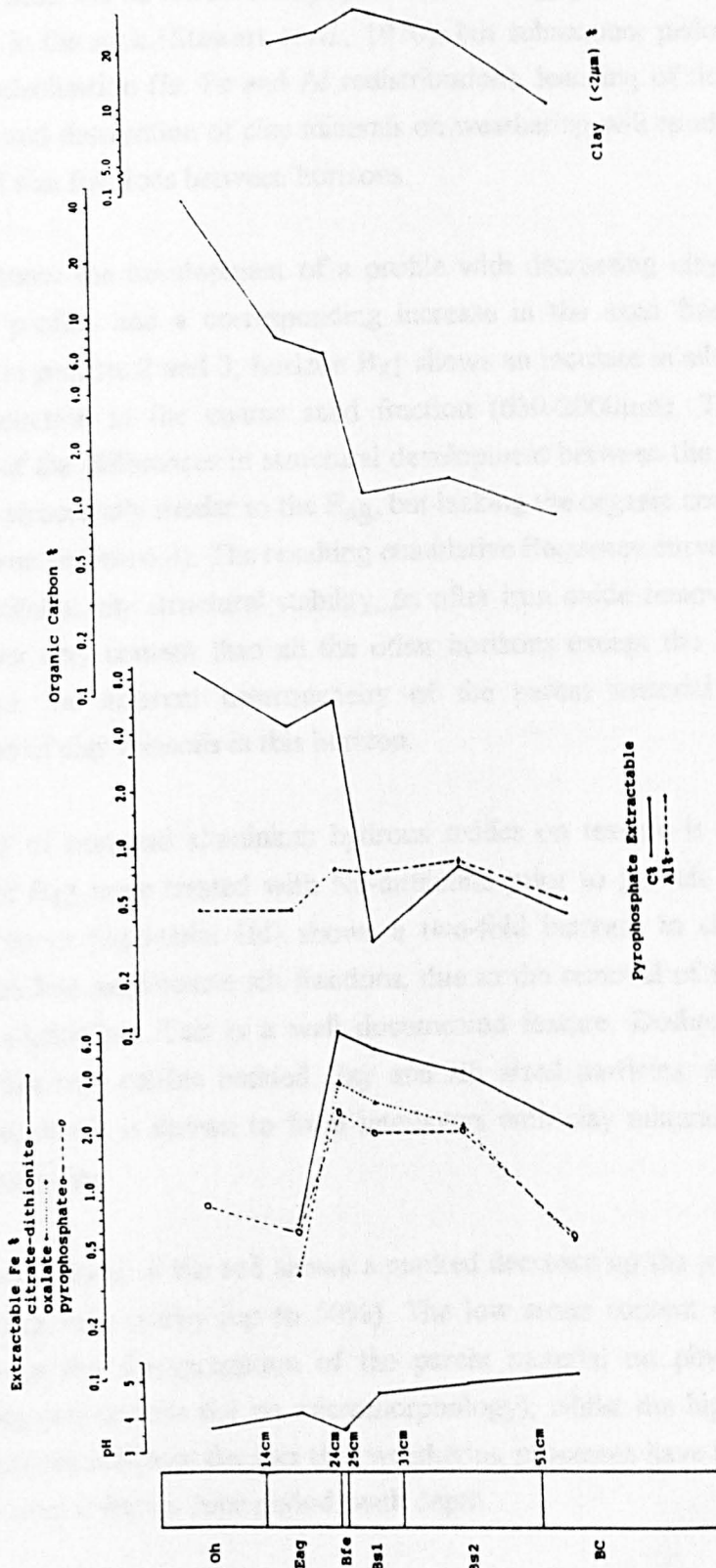


Figure 6.3 Graphic representation of the physical and chemical data for an ironpan stagnopodzol (P3). Log scales used.



Particle size distribution data for the rest of the profile show the development of textural differences with decreasing depth (Appendix II d). The generally high clay and silt content of these soils reflects the nature of the parent material, mud- and siltstones, which are composed mainly of fundamental primary particles of silt and clay size. These will be released on physical weathering, probably in the same ratio as they occur in the rock (Stewart *et al.*, 1970), but subsequent pedological processes such as podzolisation (*ie.* Fe and Al redistribution), leaching of fine particles down the profile and destruction of clay minerals on weathering will result in alterations of the ratio of size fractions between horizons.

The data show the development of a profile with decreasing clay and silt content down the profile, and a corresponding increase in the sand fraction with depth. However, in profiles 2 and 3, horizon B_{s1} shows an increase in silt and clay content with a reduction in the coarse sand fraction (630-2000µm). This is possibly a reflection of the differences in structural development between the B_{s1} and B_{s2}, the B_{s1} being structurally similar to the E_{ag}, but lacking the organic content to hold units together (see section 6.4). The resulting cumulative frequency curve resembles that of the B_{s2} without any structural stability, *ie.* after iron oxide removal. In P3 the E_{ag} has a lower clay content than all the other horizons except the BC, which is due possibly to the inherent heterogeneity of the parent material or even greater destruction of clay minerals in this horizon.

The effect of iron and aluminium hydrous oxides on texture is seen clearly when samples of B_{s2} were treated with Na-dithionite prior to particle size analysis. The resulting curve (Appendix II d) shows a two-fold increase in clay and silt and a decrease in fine sand/coarse silt fractions, due to the removal of the bonding agents iron and aluminium. This is a well documented feature. Deshpande *et al.* (1964) showed that iron oxides bonded clay and silt sized particles, and suggested that aluminium, which is known to form interlayers with clay minerals, also bound clay particles together.

The >2mm portion of the soil shows a marked decrease up the profile, with the B_{s2} and C being very stoney (up to 50%). The low stone content of the E_{ag} horizon results from the disaggregation of the parent material on physical and chemical weathering (see section 6.4 on micromorphology), whilst the high stone content of lower horizons indicates the fact that weathering processes have been less severe, or occurred over a shorter time period, with depth.

The heavy mineralogy of this soil reflects also the extent of weathering and the soil parentage (Appendix IIb). All horizons have a similar heavy mineralogy, although the abundance of chlorite is lower, due presumably to more intense weathering, in the upper horizons. There are occasional grains, such as kyanite and amphiboles, characteristic of Irish Sea and Welsh ice respectively, but these are thought to have been introduced by aeolian transport (Livesey, 1966; Bower, 1970) since in the final phase of the Late Devensian glacial period Hiraethog is thought (Livingston, 1991) to have had its own ice cap and so excluded foreign ice.

The chemical data trends for the three profiles studied are very similar (Appendix IIc). The pH values are low in the surface peaty accumulation (pH 3.5) and rise steadily with depth to around pH 5, reflecting the organic nature of the surface horizon, the acid leached nature of these soils and the movement of cations down the profile from an eluviated to illuviated horizon. The rise in pH with depth is not continuous, with the ironpan (B_f) showing a lower pH, of around 3.8, than the horizons above and below. This is due possibly to the accumulation of organic matter on the surface of the ironpan. Cation exchange capacity is highest in the eluviated E_{ag} horizon (40–44 me 100g) reflecting a higher clay (with more vermiculite) and organic matter content of this horizon, and decreases with depth due to decreasing amounts of these materials. The % base saturation, however, shows the inverse relation, increasing from around 2.5% to 6% down the profile since there are less exchange sites available at depth and so a higher percentage are occupied, even though the exchangeable cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺) are generally very low throughout the profile.

The values of organic carbon reflect the build up at the surface of a peaty horizon which, as discussed in Chapter 3, is thought to have had a role in the development of podzolic features in these soils. This horizon is designated O_h since in the literature (Rudeforth *et al.*, 1984; Avery, 1990) it is suggested that this layer is waterlogged for more than 30 consecutive days in most years, the criterion set out by SSEW (Avery, 1980). This peaty surface horizon (O_h) is around 45% organic carbon, with a sharp decline in this figure moving into the mineral soil indicating the sharp boundary between the O_h and E_{ag} horizons.

Organic carbon percentage decreases from the E_{ag} through to the C, with the E_{ag} and B_f horizons having around 5% organic C. Profile 1 shows an increase of organic C in the B_f due to the presence of a thicker root mat lying on the surface of the ironpan. Organic carbon in the E_{ag} can be explained by the downwash of organic

material, primarily down ped faces, visible when the soil dries out, which can lead to a general staining of this horizon, masking its characteristically bleached colour. High levels of organic carbon in the B_f (≈6%) reflect the accumulation of organic matter at its surface, especially in the form of a root matt when the pan is thick enough and continuous enough to prevent penetration by roots. The presence of organic carbon and pyrophosphate extractable carbon (C_p) in the lower horizons indicates that material can penetrate the iron pan, although it is likely that this consists of well humified, soluble organic acids, or that this organic C relates to material transported down the profile prior to ironpan formation. A marked increase is shown by C_p in the B horizons and this is possibly related to the podzolisation process, since organic acids are thought to complex iron, moving it down the profile to accumulate in lower horizons (Buurman and van Reeuwijk, 1984).

Table 6.1 Extractable iron ratios

Ironpan stagnopodzol:	Fe _d /Fe _o	Fe _d /Fe _p
Profile 1 : Eag	5.00	1.67
Bf	2.60	2.95
Bs1	1.86	4.91
Bs2	1.26	2.00
BC	2.00	3.20
Profile 2 : Eag	3.50	1.17
Bf	2.48	2.79
Bs1	1.96	2.75
Bs2	1.91	2.00
BC	1.82	1.82
Profile 3 : Eag	3.00	1.00
Bf	1.94	2.92
Bs1	2.04	2.75
Bs2	1.83	2.10
BC	4.00	4.00
Podzolised brown earth		
Ah	6.40	1.78
Bs1	1.73	2.37
Bs2	2.00	2.10
BC	2.06	3.89
Stagnohumic gley		
Profile 1 : Eag	5.00	1.43
Bg	8.00	0.80
BCg	-	1.25
Profile 2 : Eag	10.00	1.11
Bg	2.67	1.14
BCg	-	5.00

The analytical data obtained for "free iron and aluminium oxides" provides the diagnostic characteristics necessary to classify these soils according to the SSEW

system (Avery, 1980). Fe_O gives an indication of the quantities of amorphous iron in these soils. This shows a sharp increase with depth, peaking in the upper B_s horizons studied at around 3%, and then tailing off slightly with depth. Fe_d is thought to represent the total ferric iron content which peaks in the B_f horizon at around 6%. The E_{ag} has a very low iron oxide content ($\approx 0.7\%$), reflecting its leached and reduced state. Fe_p is thought to be that iron associated with organic carbon, and again this shows a peak in the iron pan, suggesting some iron movement is connected with the movement of humic substances as an organic complex.

Ratios of Fe_d/Fe_p and Fe_d/Fe_O are often used to assess the relative quantities of iron in its different forms (Campbell and Schwertmann, 1984; Table 6.1). Fe_d/Fe_O ratios decrease with depth, suggesting an increase in the proportions of amorphous materials in the B horizons, whilst Fe_d/Fe_p ratios peak in the B_f or upper B_s indicating a lower proportion of humic acid/Fe complexes in these horizons than those above or below, with the lowest ratios being found in the E_{ag} and B_{s2} horizons. This is suggestive of the fact that although some iron may be mobilised and transported by organic molecules, the situation in these soils is more complicated. In the E_{ag} horizon, there is little Fe_d and a high organic C content, and as such one would expect much of the iron that was being released by weathering to be complexed by organic molecules. In the B_f , the ratio Fe_d/Fe_p rises sharply. This would indicate that this feature is relatively stable and that the iron is aged, more crystalline and, due to the indurated nature of the pan, possibly only undergoes additions of iron and organic matter on its upper surface. The B_{s1} shows a very similar trend, with equal or higher Fe_d/Fe_p ratios. From analyses of the iron content of the clay fraction (Appendix IIg), the B_{s1} appears to have more iron concentrated in a larger size fraction, which may make it unavailable for organic complexation. This would suggest that there is little input of new iron into this horizon, a possibility also raised from clay mineralogical and micromorphological studies (sections 6.3 and 6.4). Lower down the profile ratios decrease which suggests that a larger proportion of iron in the B_{s2} and BC is associated with organic matter and that these horizons are more active.

The extractants NaOH and dithionite-citrate were employed to study the amorphous materials in the clay fraction of these soils, as well as cleaning this material for XRDA (Appendix IIg). Dithionite-citrate extraction removed relatively large amounts of Fe, as well as Al and Si, from the clay fraction in the ironpan stagnopodzol. The B_{s2} released $>10\%$ Fe_d , more than the bulk soil, suggesting that in this horizon iron is concentrated in this fraction, whilst less is so concentrated in the B_{s1} and E_{ag}

horizons. Si was extracted in the range of 1.2-2.0mg/g clay (48-80mg H₄SiO₄/l). Rezk (1975), in a review of the literature, stated that solutions with a pH<9 in equilibrium with amorphous silica contain between 120mg/l to 140mg/l H₄SiO₄. Since the amounts of soluble silica extracted with dithionite were less than the upper limits of its solubility the volume used in the present extraction was not a limiting factor, and so the amounts obtained probably represent silica that had been chemically bonded and occluded in the Fe and Al hydrous oxides, particularly the "free iron oxides".

There is a noticeable difference in the response of Al and Si to dithionite-citrate and NaOH extractions due to the complexing of Al by citrate, thereby extracting more, whilst there was a large increase in silica solubility with the pH increase associated with the NaOH extraction. However, overall, less silica was extracted than Al in both systems, and Rezk (1975) suggested three possible reasons for the low concentration of silica extracted from soils. However he stressed that, although it is difficult to determine which may be active within a soil, there is no anomaly in the fact that these three processes may occur in the same soil so making it difficult to separate them. The three reasons given are: (i) silica is released by hydrolysis during weathering and so may be lost in the drainage water; (ii) silica released may polymerise to form a silica gel or be incorporated into pedogenic minerals or bioliths; (iii) silica release may be inhibited by Al/Fe coatings.

The (Fe_p + Al_p) in the B_s horizon amounts to >5% of the clay content confirming its spodic character and this, along with the other analytical data, would place this soil in the "ironpan stagnopodzols" (Hiraethog series) in the classification scheme of the S.S.E.W. (Avery, 1990) and in the typic plaquaquod class of the U.S.D.A. classification (Avery, 1990).

6.2.2 Cambic Stagnohumic Gley

The parent material from which these profiles developed is very similar to that described for the stagnopodzol. The heavy mineralogy indicates that the source of this material is again local (*ie.* Silurian silt- and mudstones). The texture, however, is different. The coarse sand and silt fractions are lower and the fine silt and clay fractions larger (fig. 6.4). This may be a result of the difficulty in sampling at depth because of the indurated nature of the lower horizons, so that sampling took place higher up the lowest horizon in more altered material. The saturation of these profiles may also have aided the physical disaggregation of the parent material into finer

constituents, and many of the rock fragments sampled from the B_g were soft and could be crushed by hand.

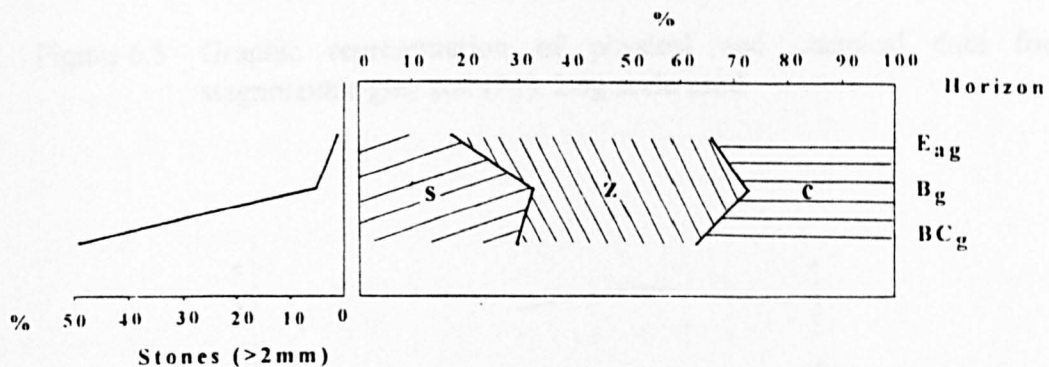


Figure 6.4 Summary of particle size analysis of a stagnohumic gley profile (P1) including % stone (>2mm) content.

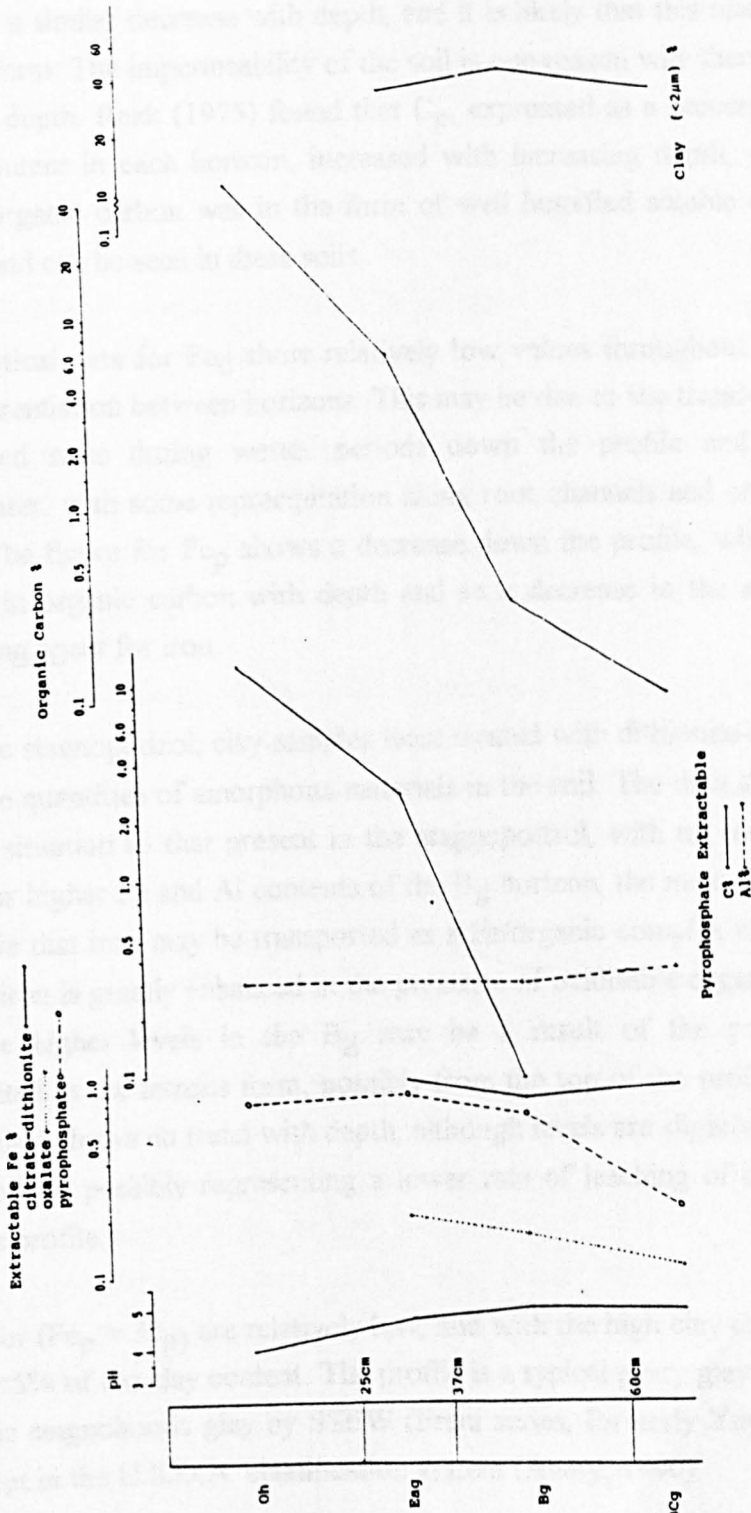
Particle size distribution reveals that up to 80% of particles are concentrated in the silt and clay fractions, with the highest percentages in the surface E_{ag} horizon (Appendix II d). There is a slight increase in the clay fraction in the B_g or BC_g horizons, and this is due to heterogeneity of the parent material (banding as described by Warren *et al.*, 1984). It is unlikely that the cause is clay translocation and redistribution since from the micromorphological investigation argillans are consistently <0.5%. Sand and stone content increases with depth resulting from less intense weathering and alteration of the parent material. However, doubts are raised concerning the value of the % >2mm figures. During the micromorphological investigation it was noticed that some unsuspected stone fragments were visible by a slight difference in the fabric. In the field, these stones were soft and had been completely weathered, and in the grinding and sieving of the soil it is likely that some of these fragments disintegrated.

The chemical analytical data show a strong to moderate acidity throughout the profile, rising from pH3.8 to pH5.0 in the lower horizons, the pH in the top 40cm being due to the peaty nature of the material. As in the Hiraethog series, the CEC is highest in the surface E_{ag} horizon due to high clay (vermiculite) and organic matter content with the percentage base saturation showing an inverse relationship and rising to ≈7% in the BC_g horizon due to a reduction in the available exchange sites. The levels of exchangeable cations are generally low throughout the profile.

The prevailing soil conditions (impeded drainage, high acidity, very low base saturation) together with the present-day climatic conditions, allow the accumulation

of peat at the surface. The data for organic carbon reflects this, with very high levels (up to 46%) in the surface O_h horizon, with percentages falling with depth.

Figure 6.5 Graphic representation of physical and chemical data for a stagnohumic gley soil (P1). Log scale used.



The E_{ag} horizon has up to 6% organic carbon, and this is likely to be due to the downwash of material, staining the horizon and especially the surfaces of cracks which develop when the soil occasionally dries out during the summer months. Rezk (1975) also showed differences in the organic content of the horizons within the peat (L, F and H). These are probably due to differences in the degree of humification of the material, the peat usually being more humified with depth and, therefore, age.

C_p shows a similar decrease with depth, and it is likely that this material is in a well humified form. The impermeability of the soil is one reason why there is little organic carbon at depth. Rezk (1975) found that C_p , expressed as a percentage of the total carbon content in each horizon, increased with increasing depth, suggesting again that the organic carbon was in the form of well humified soluble organic acids. A similar trend can be seen in these soils.

The analytical data for Fe_d show relatively low values throughout the profile, with little differentiation between horizons. This may be due to the translocation of iron in its reduced state during wetter periods down the profile and its loss in the groundwater, with some reprecipitation along root channels and cracks during drier phases. The figure for Fe_p shows a decrease down the profile, which relates to the decrease in organic carbon with depth and so a decrease in the availability of this complexing agent for iron.

As for the stagnopodzol, clay samples were treated with dithionite-citrate and NaOH to analyse quantities of amorphous materials in the soil. The data show a completely different situation to that present in the stagnopodzol, with no real trends obvious, except for higher Fe and Al contents of the B_g horizon, the most mottled horizon. It is possible that iron may be transported as a Fe/organic complex since the reduction of ferric iron is greatly enhanced in the presence of oxidisable organic substances. As such, the higher levels in the B_g may be a result of the precipitation of Fe translocated in the ferrous form, possibly from the top of the profile in the drainage water. Silica shows no trend with depth, although levels are slightly higher than in the stagnopodzol, possibly representing a lower rate of leaching of dissolved materials from this profile.

Values for $(Fe_p + Al_p)$ are relatively low, and with the high clay contents this put the total at <5% of the clay content. The profile is a typical peaty gley soil, designated as a Cambic stagnohumic gley by SSEW (Freni series, formerly Ynys) and as a Histic Cryaquect in the U.S.D.A. classification system (Avery, 1990).

6.2.3 Typical Brown Podzolic Soil.

Avery (1990) includes in the Podzolic Brown Soils Group most of the well drained acid soils previously grouped as "brown podzolic" in England, Wales and Ireland (Avery, 1980), "brown forest soils" in Scotland and as "upland" or "podzolic brown earths" by the Forestry Commission. The parent material for this profile is very similar to that of the stagnopodzol, high stone and sand content with stones oriented in the direction of the slope (fig 6.6), indicating that this is a periglacial "head" deposit.

The particle size distribution curves for the profile (Appendix II d) show very low clay contents in both the A_h and BC horizons, whilst the B_s has very high quantities of both silt and clay, totalling up to 70% of particles of <2mm in size. The upper horizon has only 5% clay, and these differences are due either to the build up of amorphous materials in the B_s , or to the movement of clay-sized materials down the profile, although there is no evidence to support the latter since few argillans were visible in thin-sections of this horizon. The removal of Fe and Al oxides by citrate-dithionite from the B_s further boosts the quantities of clay and silt sized particles, again indicating the capacity of Fe and Al oxides to bind soil particles together.

The >2mm soil fraction is higher in the A_h than in the B_s horizon, the reverse of that seen in both the stagnogley and stagnopodzol, due possibly to input of >2mm stones from the slope above. The heavy mineralogy of this profile does, however, indicate that it is again formed on a parent material of local origin.

The chemical analytical data show an acidic profile with the pH rising from pH4.3 to pH5.1 at depth, reflecting its leached nature, but the profile lacks a peaty surface horizon, in contrast to the other soil series studied. The C.E.C. is highest in the surface A_h horizon due to the high organic matter content and falls steadily down the profile. As with the other profiles, the % base saturation shows the inverse relationship, increasing from 3.5% to 6% with depth due to the lower availability of exchange sites, although as before the quantities of exchangeable cations are generally low throughout the profile. The values for organic carbon decrease markedly from the A_h to the upper B_s horizon, indicating the organic nature of the former horizon, although lower down in the B_s the organic carbon content increases slightly. This is also the case for the values for Fe_p , suggesting that some of the iron in the B_s is associated with organic carbon.

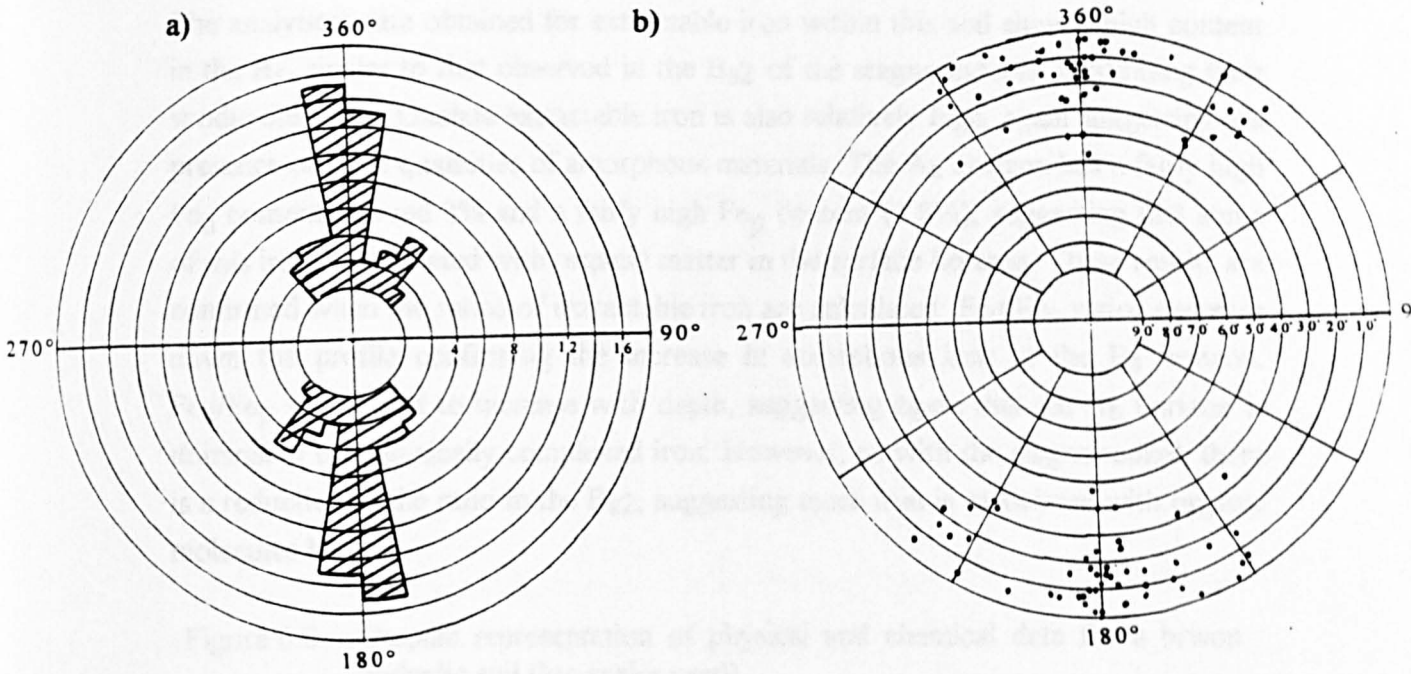


Figure 6.6 Fabric analysis of the parent material of a typical brown podzolic soil (a) rose diagram showing the preferred long axis in 10° classes (b) the direction and angle of plunge of the long axis, each dot representing one stone. Slope direction is S.

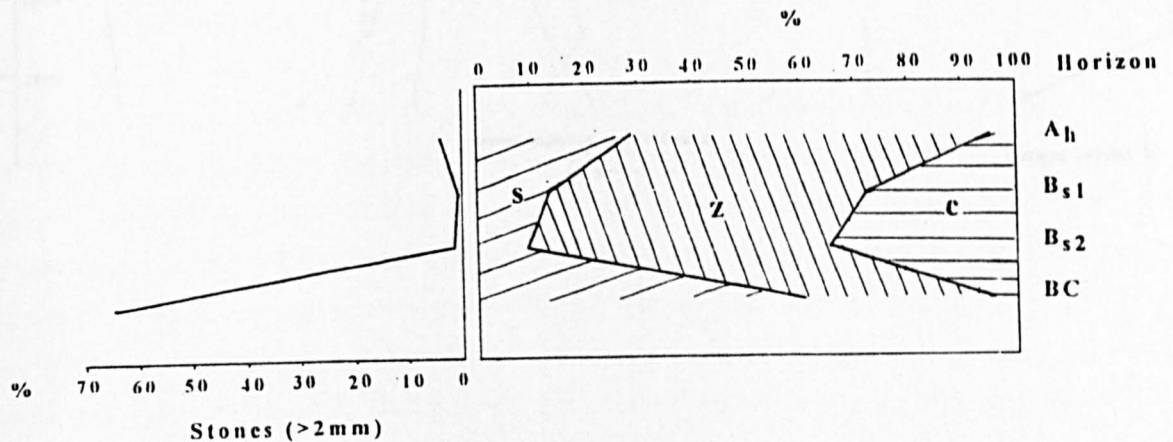
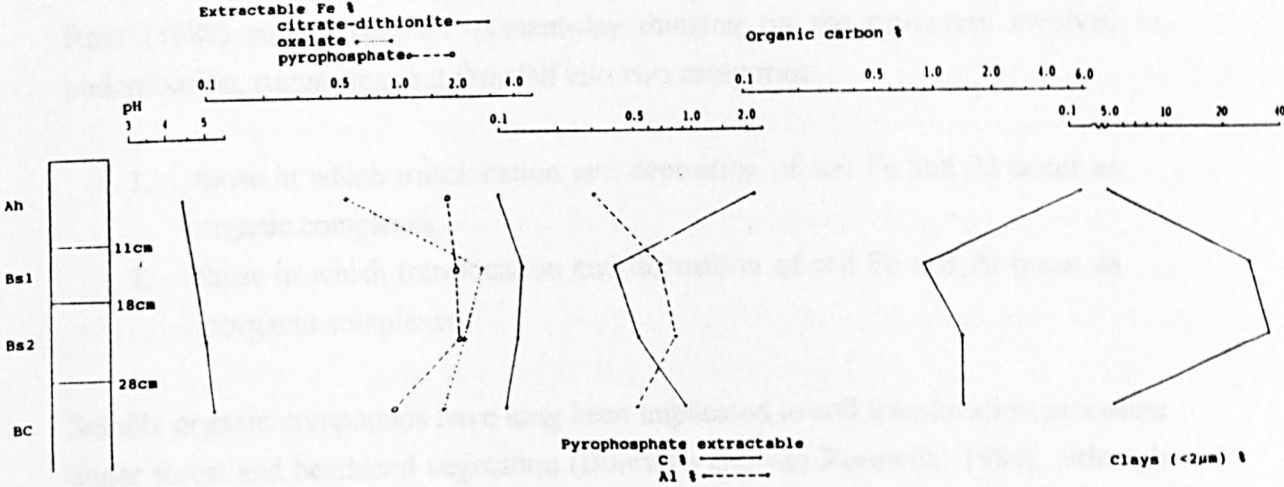


Figure 6.7 Summary of the particle size analysis of a typical brown podzolic soil including % stone (>2mm) content.

The analytical data obtained for extractable iron within this soil show a high content in the B_s, similar to that observed in the B_{s2} of the stagnopodzols, confirming their spodic character. Oxalate extractable iron is also relatively high, again suggesting the presence of large quantities of amorphous materials. The A_h horizon has a fairly high Fe_d content, around 3% and a fairly high Fe_p content (1.8%), suggesting that some of this iron is associated with organic matter in the surface horizon. These results are confirmed when the ratios of extractable iron are calculated. Fe_d/Fe_o ratios decrease down the profile confirming the increase in amorphous iron in the B_s horizon. Fe_d/Fe_p ratios tend to increase with depth, suggesting again that the A_h horizon is dominated by organically complexed iron. However, as with the stagnopodzol, there is a reduction in the ratio in the B_{s2}, suggesting more iron is associated with organic molecules here.

Figure 6.8 Graphic representation of physical and chemical data for a brown podzolic soil (log scales used).



The trends shown in terms of extractable Fe, Al and Si from the clay fraction relating to amorphous materials within these soils are similar to those seen in the stagnopodzol. Extractable Si quantities are higher in the brown podzolic soil B_s horizon than in the B_s of the ironpan stagnopodzol. Since the <2µm fraction is also greater, this possibly represents a greater accumulation of amorphous materials in the

brown podzolic soil. However, iron does not show the extreme differentiation between the upper and lower B_s. This is due to the lack of a waterlogged peaty surface horizon, since as peat accumulation continues so its influence will extend to greater depths within the profile. Aluminium is again concentrated in the B_s and Rezk (1975) suggests this is due to the translocation of Al and the subsequent accumulation of "Al₂O₃" in the B horizon. One difference between this soil and the stagnopodzol is the amount of iron extractable from the clay fraction of the B_s. It is higher (>11%), whilst Fe_d is lower in the B_{s1} than in the same horizon in the stagnopodzol. This suggests that an even higher proportion of iron is concentrated in the clay fraction in this soil, and this may account for the high clay % values noted earlier.

These features characterise this soil as a typical brown podzolic soil (Manod series) in the SSEW classification or as a typic ochrept (USDA) after Avery (1990).

6.2.4 Conclusions

Ross (1989) summarised the present-day thinking on the processes involved in podzolisation, suggesting that they fall into two categories:

1. those in which translocation and deposition of soil Fe and Al occur as organic complexes;
2. those in which translocation and deposition of soil Fe and Al occur as inorganic complexes.

Soluble organic compounds have long been implicated in soil translocation processes under forest and heathland vegetation (Buurman and van Reeuwijk, 1984), although there is some debate as to the relative importance of simple organic compounds (polyphenols) derived from leaf and litter washings, and more complex and high molecular weight organic compounds (humic and fulvic acids). However, the discovery of imogolite-type allophanes in podzolic B horizons has seriously questioned whether organic compounds play an important role in Fe and Al translocation in podzolic profiles (Farmer, 1984).

Certain conclusions can be drawn from the data presented here. The three soil types described are all formed on similar parent materials, the podzols developing in "head" deposits of Silurian silt- and mudstone, which have a high stone and low clay content, the stones being angular in shape reflecting the effects of physical, but not chemical,

weathering. The heavy mineralogy suggests a similar situation, being dominated by chlorite, tourmaline, opaques, rutile and zircon, a suite of minerals characteristic of this rock type. However, the soils of Hiraethog exhibit striking physical and chemical differences as well as different profile morphologies. Ironpan stagnopodzols have a surface peaty horizon, a bleached acidic E_{ag} lacking in significant quantities of iron hydrous oxides with an underlying B_s rich in Fe and Al hydrous oxides and amorphous materials. This B_s shows differences, on physical and chemical criteria, between upper and lower portions, a feature not so prominent in the brown podzolic soil. The stagnohumic gley soil lacks these high levels of Fe or Al hydrous oxides, and has a heavier texture suggesting more breakdown and/or heterogeneity of the parent material. This is a situation very similar to that presented in the literature (Rudeforth *et al.*, 1984; Avery, 1990).

From this similar starting point, the three series have developed. The stagnohumic gley soil has very low levels of Fe and Al hydrous oxides and a heavy texture. This suggests that physical and chemical weathering have acted to disaggregate the parent material to its constituent prime particles, silts and clays, and it is likely that differences in texture down profiles and between profiles may be due to the initial heterogeneity of the parent material. The low slope angle, inherent small pore size and the accumulation of organic matter at the surface have led to the development of gley conditions in these soils, leading to the release and loss of Fe and Al in the groundwater, resulting in a pale soil colour. Root channels and cracks will serve as passageways for air into the soil resulting in re-oxidation of ferrous iron and manganese and mottling of the soil. The absence of ferric hydrous oxides in sufficient quantities also prevents the stabilising of any structural units which form, accentuating the problems of poor drainage and gleyed conditions.

The stagnopodzol has a better drained B horizon as indicated by its redder colouration. Ferric hydrous oxides present in this horizon will help stabilise the structural units formed and therefore maintain the well drained conditions. The Fe and Al hydrous oxides concentrated in the B_s will have come from the chemical weathering of minerals, such as chlorite, which are less abundant in the surface horizon of this soil as compared to that in the stagnogley, suggesting more intense weathering of this horizon. The surface of the stagnopodzol is, however, also subject to gleying, but rarely shows signs of mottling, due possibly to the almost complete removal of iron from this horizon. Avery (1990) reported on volumetric physical analyses on core samples collected from E_{ag} horizons which showed an unusual combination of low bulk density and very small air capacity, indicating that there are

few coarse ($>60\mu\text{m}$) pores but many in the size range emptied between 0.1 and 2 bars ($30\text{-}1.5\mu\text{m}$).

The textural development in the stagnopodzol reflects the greater intensity of weathering in this profile as compared to the stagnogley. This is also noted from the reduction in relative amounts of chlorite in the heavy mineral fraction, least amounts being found in the E_{ag} , and this is augmented by evidence from clay mineralogy as will be described in section 6.3. However, the B_{s1} is more similar to the E_{ag} in texture than to the B_{s2} , with similar or greater quantities of clay and silt-sized particles, although the B_{s2} , when treated with dithionite-citrate to remove Fe and Al hydrous oxides, also has a textural make-up similar to the B_{s1} . This would suggest that the higher quantities of clay and silt detected were due to a lack of bonding by Fe and Al in the B_{s1} . However, the B_{s1} has more Fe_d and Fe_o than the B_{s2} : the answer to this apparent contradiction lies with the microstructure (see section 6.4). The B_{s2} has an open spongy fabric, whilst the microstructure of the B_{s1} is more sub-angular blocky, with iron concentrated as nodules which will therefore not have such an impact on the stability of the structure. This is backed up by the fact that the B_{s2} contains higher quantities of Fe_d in the $<2\mu\text{m}$ fraction, whilst the B_{s1} has Fe concentrated in the $<2\text{mm}$ fraction.

This will also have implications for the clay mineralogy, since it has been shown that Fe and Al hydrous oxides can protect clay minerals from weathering (Wang *et al.*, 1989). This will obviously be less effective if such hydrous oxides are concentrated into nodules. The greater quantities of Fe_o , (*ie.* amorphous), in the B_{s1} may reflect a greater intensity of chemical weathering in this horizon. This distinction between the B_{s1} and B_{s2} is not apparent in the brown podzolic soil, with this profile having Fe concentrated in the $<2\mu\text{m}$ fraction throughout the B_s . It is thought that podzolised brown earths may be members in a continuum between brown earths and stagnopodzols (Avery, 1990), and as such the formation of an organic surface and an eluviated E_{ag} horizon may result in this differentiation of the B_s .

Quantities of the different extractable forms of iron can be used to supply information on the translocation processes occurring in these soils. The stagnogley has very low quantities of iron ($<1\%$), although more is found in the $<2\mu\text{m}$ fraction in the B_g horizon. Fe_d/Fe_o ratios are high, suggesting that amorphous materials play little part in the development of these soils, whilst Fe_d/Fe_p ratios are low, especially in the upper horizons, suggesting that organic molecules are associated with iron. This is

very clear in thin sections, where many root residues are found in voids with iron hypocoatings (see section 6.4).

A very different picture emerges from the stagnopodzol profiles. In these, Fe_d/Fe_o ratios decrease with depth, suggesting accumulations of aged amorphous forms of iron. Fe_d/Fe_p ratios peak in the B_f or B_{s1} horizons, suggesting that these are composed of crystalline iron and are thus not receiving iron moved by organic complexes; this is highlighted by the clay mineralogical investigation (see section 6.3). This could relate to the lack of iron in the surface horizon. However, levels of Fe_p do peak at the B_f which may represent iron associated with the organic accumulations at the surface of the pan.

Lower down the profile, the B_{s2} can have a low Fe_d/Fe_p ratio. Pyrophosphate is known to extract organically fixed iron, but will also remove amorphous gel forms. The B_{s2} has iron concentrated in the $<2\mu m$ fraction, and this may therefore relate to a movement of iron from the B_{s1} to the B_{s2} , since the B_{s1} has iron concentrated in the larger size fractions. This differentiation is not so clear in the brown podzolic soil, which would suggest that it is due to the development of the peaty surface (O_h) horizon, leading to increased weathering at the surface along with increased waterlogging, resulting in continued redistribution of iron down the profile. No differentiation in Al_p can be detected, but this may be a result of the lower complexing ability of organic matter for Al as compared to Fe.

Thus, the suggestion that ironpan stagnopodzols may be an end member of a series seems to be confirmed by these data. The three soil types all began as very similar material, but due to differences in relief and drainage, have developed into distinct soil series. However, from the data available it is not possible to support either theory of podzol development in terms of the organic/inorganic agents responsible for iron and aluminium translocation.

6.3 Clay mineralogy

XRDA traces for the ironpan stagnopodzol (P3), the stagnohumic gley soil (P2) and the brown podzolic soil (P1), the parent material and minerals concentrated magnetically are presented in Appendix III. All profiles sampled for physical and chemical analyses were studied in terms of their clay mineralogy, and where differences between profiles of the same soil series occur, these will be noted in the discussion. The minerogenic sediments from the Cefn Mawr peat core and the Llyn y

Foel-frech lake core were also analysed, and the traces for these are presented in Appendix IIIf.

6.3.1 Parent material (Silurian mud- and siltstone)

Table 6.2 Summary of the peaks of minerals present in the parent material (Brindley and Brown, 1980).

Mineral	XRDA peaks
Chlorite	1.42nm(001); 0.71nm(002); 0.472nm(003); 0.354nm(004); 0.284nm(005); 0.259nm(202); 0.254nm(201)
Hydrous mica	1.0nm(002); 0.5nm(004); 0.45nm(110); 0.439nm(021); 0.39nm; 0.37nm; 0.35nm; 0.32nm; 0.299nm; 0.287nm; 0.280nm; 0.250nm
Feldspar	0.68nm; 0.407nm; 0.415nm; 0.38nm; 0.262nm
Quartz	0.43nm; 0.247nm; 0.23nm
Magnetite	0.295nm; 0.242nm
Rutile	0.322nm

Analysis of the parent material by XRD gives an idea of the overall mineralogy of the rock, not just its clay mineralogy. Quartz dominates with peaks at 0.23nm, 0.247nm, 0.335nm and 0.43nm, showing no preferred orientation (ratio of peaks = 1.05) in relation to the cleavage .e. in samples cut parallel and perpendicular to the cleavage (see section 5.3.8). Trioctahedral Fe-rich chlorite, with peaks at 1.42nm, 0.71nm, 0.47nm, 0.35nm, 0.28nm, 0.26nm and 0.254nm is orientated parallel to the cleavage (2.3), as is hydrous mica (5.2) which gives peak heights of about double that of chlorite. The remainder of the mineralogy shown is composed of feldspar and magnetite with some rutile. Feldspars give peaks intermediate between 0.422nm and 0.403nm (Brindley and Brown, 1980). Peaks are noted between 0.318nm and 0.322nm suggesting these are plagioclases and not K-feldspars.

It is interesting to note that the chlorite is less well orientated parallel to the cleavage than hydrous mica. This is also seen in thin sections with sand-sized chlorite grains which are not usually orientated completely parallel to the cleavage of rock fragments. In traces from samples cut parallel and perpendicular to the cleavage the 1.0nm peak of hydrous mica is asymmetrical. If half peak height width is given the value of 1.0, the ratio of left:right side at half peak height is 1.4, suggesting possible

vermiculatisation of this mineral. It is slightly more in the peak from a section cut perpendicular to the cleavage.

Table 6.3 Summary table of minerals present in clay fractions (<2µm esd)

NB1

Chl. = Chlorite

HM = Hydrous mica

V. = Vermiculite

V./HM = Vermiculite/hydrous mica interstratified mineral

Chl./HM = Chlorite/hydrous mica interstratified mineral

HIV = Hydroxy interlayered vermiculite

Q. = Quartz

Lep. = Lepidocrocite

Goe. = Goethite

Rut. = Rutile

Mineral ¹	Chl.	HM	V.	V./HM	HM/Chl.	HIV	Q.	Lep.	Goe.	Rut.
Sample										
Stagnopodzol										
E _{ag}		+++	++	++		+	+++			+
B _f		+++	++	++		+	+++	++	+	+
B _{s1}		+++	+++	++		+	+++	++		+
B _{s2}	++	+++	+	++		+	+++	+		+
BC	+++	+++		+			+++			+
Stagnogley										
E _{ag}	+	+++	+	+		+	++			
B _g	++	+++	+	+			+++			
BC _g	+++	+++	+	+		+	+++			
Brown podzolic soil										
A _h	+	+++	++	++			+++	+		+
B _{s1}	++	+++	+	+++			+++	+		+
B _{s2}	++	+++	+	+++			+++	+		+
BC	++	+++	+	+++			+++	+		+
Cefn Mawr 410cm	++	+++	+	++						
LYFF										
215cm	+++	+++			++					
235cm	+++	+++			++					
250cm	+++	+++			++					
300cm	+++	+++			++					
320cm	+++	+++			++					

Table 6.4 Presence/absence of vermiculite. *ie.* $\frac{1.0\text{nmK}/1.4\text{nmK}}{1.0\text{nmMg}/1.4\text{nmMg}}$

Sample	Untreated.	Treated (0.5N NaoH)
Stagnopodzol		
Eag	9.2	5.9
Bf	2.6	
Bs1	4.0	18.1
Bs2	1.3	4.6
Bs2DT	1.5	1.8
BC	1.1	1.0
Stagnogley		
Eag	1.4	2.6
EagDT	1.5	1.6
Bg	1.9	1.3
BCg	1.7	1.2
Podzolised brown earth		
Ah	2.2	5.6
Bs1	1.5	2.9
Bs2	1.1	8.0
Bs2DT	1.4	6.5
BC	1.2	2.5
Cefn Mawr		
410cm	1.4	-
LYFF		
215cm	1.0	-
235cm	1.0	-
250cm	1.0	-
300cm	1.0	-
320cm	1.0	-

NB1. No vermiculite - ratio = 1.0

All vermiculite - ratio = infinity

Table 6.5 Amorphous materials (extractable) from clay fraction. Figures shown are the means from each soil series as % of the clay fraction.

Sample	0.5M NaOH			Citrate-dithionite		
	Si	Al	Fe	Si	Al	Fe
Stagnopodzol						
Eag	0.31	1.53	0.18	0.20	0.56	0.37
Bs1	0.28	1.51	0.32	0.16	1.54	3.41
Bs2	0.29	1.89	0.76	0.13	3.73	9.79
BC	0.17	1.68	0.24	0.20	1.59	5.01
Stagnogley						
Eag	0.42	2.13	0.08	0.06	0.45	0.64
Bg	0.48	2.73	0.14	0.15	0.44	2.20
BCg	0.44	2.89	0.09	0.16	0.46	0.84
Podzolised brown earth						
Ah	0.43	1.44	0.18	0.06	1.69	11.20
Bs1	0.47	2.60	0.24	0.13	1.21	11.52
Bs2	0.34	2.24	0.30	0.12	1.30	11.52
BC	0.18	2.40	0.22	0.12	1.33	8.88

6.3.2 Ironpan Stagnopodzol

Clay samples prepared using the methods described in section 5.3 were run from each horizon (Eag, Bs1, Bs2 and BC) for three profiles before and after treatment to remove amorphous materials. The three main types of clay minerals found in this soil were chlorite, hydrous mica and vermiculite, as well as interstratified minerals.

The BC horizon traces compare well with those of the parent material, indicating that this material is physically, but not chemically, weathered. There is little difference between treated and untreated samples suggesting an absence of amorphous material, again due to the lack, or low intensity, of chemical weathering with only physical weathering bringing about disaggregation. This horizon is dominated by hydrous mica and chlorite, with the chlorite being stable when heated to 550°C; vermiculite is not detected in this horizon. Lepidocrocite, with a peak at 0.63nm, is absent, reflecting the relatively unweathered nature of the material. A peak at 0.89nm appears in treated samples when heated to 550°C. Since it does not appear in other horizons it is unlikely to be an artefact due to the process itself, but may be a second order peak of an irregularly interstratified mineral.

The division of the B_s into an upper and lower part (B_{s1} and B_{s2} respectively) highlighted some clay mineralogical differences. Traces, when run at the same c.p.s., are more prominent when treated to remove amorphous materials than compared to untreated clays, suggesting the presence of significant amounts of amorphous materials in this horizon. This is indicated from the data on extractable amorphous materials (Table 6.5). Both NaOH and citrate-dithionite removed the greatest total quantities of amorphous Si, Al and Fe from the B_{s2} horizon. This included up to 10% Fe_d , greater than the amount extracted from a bulk sample. This indicates that Fe is concentrated in the $<2\mu m$ fraction. All B_{s2} horizons contain chlorite whose 1.42nm peak is stable under heat treatments, although in profiles 1 and 3, when untreated, the 1.4nm peak is reduced on heating. Chlorite is also present in the $<0.2\mu m$ fraction of the B_{s2} but collapses on heating to 550°C, indicating the instability of chlorite in the smaller size fractions as suggested by other workers (Bain and Duthie, 1984). However, this instability is not noticed in the cleaned samples, suggesting the 1.4nm peak may be masked to some extent by amorphous materials. Many workers have suggested a role for amorphous Fe and Al in podzolic B horizons in coating and so protecting clay minerals from weathering (Wang *et al.*, 1989). This may also prevent their detection, especially when in low concentrations. When these amorphous materials are removed from these horizons the 1.4nm peak is more noticeable, suggesting that this is the case in these soils.

Hydrous mica is present in this profile and its 1.0nm peak remains unaffected by differing treatments. Vermiculite is now present, the basal spacings varying according to the nature of the interlayer cation and the state of hydration. Vermiculites can be detected by comparing the ratios of the 1.0nm/1.4nm peaks for the Mg^{2+} saturated and the K^+ saturated samples. Vermiculite is indicated in all the B_{s2} horizons studied, although the further reduction of the 1.4nm peak in untreated samples from profiles 1 and 3 on heating K^+ saturated samples may relate to the presence of a chlorite-like mineral such as hydroxy-interlayered vermiculite (HIV) (Barnhisel and Bertsch, 1989). It is suggested by Barnhisel and Bertsch (1989) that as the degree of filling of the interlayer space with hydroxy polymers approaches completeness so it becomes more difficult to distinguish this mineral from chlorite. He also suggested that the greater the degree of filling the higher the temperature needed to cause the collapse (or partial collapse) of HIV. In these samples collapse had occurred when samples were heated to 350°C, although no intermediate temperatures were used.

The B_{s2} contains an interstratified mineral with peaks at 1.2nm and 2.4nm relating to regularly interstratified vermiculite/hydrous mica. These peaks collapse to 1.0nm upon

K⁺ saturation and heating. It is difficult to be certain that there is no irregularly interstratified vermiculite/hydrous mica present since this may also give a peak at 1.2nm. The Bs2 also contains lepidocrocite (0.63nm) which is lost with dithionite treatment.

The upper B_s (B_{s1}) has a fairly similar mineralogy, with hydrous mica, vermiculite and regularly interstratified vermiculite/hydrous mica all present. However, the chlorite in all samples studied, as well as the <0.2μm fraction, is present in much smaller proportions with the 1.4nm peak being reduced or completely lost on heating K⁺ saturated samples, suggesting the mineral may not be chlorite but a weathering product, HIV. The presence of lepidocrocite in this horizon is more marked than in the B_{s2}, suggesting a more hydromorphic influence on this horizon, possibly due to the saturated surface organic horizon. The quantity of amorphous extractable Si is very similar to that of the B_{s2}, as is NaOH extractable Al, although Al_d and extractable Fe are only about a third of that extracted from the B_{s2}. However, in the bulk sample analyses, Fe_d is greater in the B_{s1}, suggesting that a greater proportion of iron in the B_{s1} is in the <2000μm>2μm fraction, whilst the opposite is true of the B_{s2}.

The B_f horizon has a clay mineralogy similar to that of the B_{s1}. Chlorite is absent, and the clay fraction is dominated by hydrous mica, vermiculite and a vermiculite/hydrous mica interstratified mineral. HIV is present, as is lepidocrocite and goethite. However, when comparing traces for magnetically concentrated minerals, the B_f does not give a 1.4nm peak whereas the B_{s1} does. This indicates that it is possibly an apparent lack of chlorite in the B_{s1}, with low quantities being present which are easily masked, whilst in the B_f there is almost no chlorite actually present. However, heat treatment of the K⁺ saturated samples from the B_{s1}, as described, results in a collapse of the 1.4nm peak, indicating that this is not chlorite but HIV.

The E_{ag} horizon is dominated by hydrous mica and regularly interstratified vermiculite/hydrous mica since all peaks collapse to 1.0nm on K⁺ saturation and heating. All profiles show a slight 1.4nm peak on Mg⁺⁺ saturation, but this collapses on K⁺ saturation (vermiculite) and on heat treatment of K⁺ saturated samples, indicating the presence of HIV. Lepidocrocite is absent from this horizon due to the reduced and leached state of the material.

All horizons show a peak at 1.12nm, which remains unaltered after DMSO treatment indicating that it is not due to kaolinite. This peak is also visible in the parent material

when samples cut parallel to the cleavage were scanned, and is therefore possibly due to a phyllosilicate.

6.3.3 Stagnohumic gley

The BC_g horizon of these two profiles is more weathered than that of the stagnopodzol, with hydrous mica, chlorite and vermiculite all present, although this may only represent the difficulty of sampling at depth due to the indurated nature of the lower horizon. The chlorite is, however, stable and does not collapse on heating. The B_g horizon is again very similar, although it contains an interstratified minerals, regularly interstratified vermiculite/hydrous mica. The main difference between the gley and the podzol profiles is the presence of stable chlorite in the surface mineral horizon of the stagnogley suggesting a less intense weathering regime in these profiles.

The chlorite in the <0.2µm fraction of the Eag horizon does, however, collapse on heating, indicating the instability of chlorite in the smallest size fraction. Although these profiles are dominated by hydromorphic conditions, with the presence of lepidocrocite reported in mottled horizons (Campbell and Schwertmann, 1984), this mineral is not shown on XRD traces suggesting the mineral, if present, is in quantities too small to be detected by this method from bulk samples. Extractable amorphous materials in all horizons occur in fairly similar quantities, with over 5x less Fe than in the podzolic B_{s2}. However, Si and Al occur in greater quantities due possibly, as discussed earlier, to a less intensely leached system.

6.3.4 Typical brown podzolic soil

The traces for the BC horizon are less "clean" than those for the corresponding horizon in the stagnopodzol or stagnogley. This possibly represents the fact that this is a much shallower profile and so accumulations of amorphous materials will occur proportionally lower down the profile.

The BC horizon is dominated by hydrous mica and chlorite, which is in a stable form. Vermiculite is also present as a regularly interstratified hydrous mica/vermiculite mineral which collapses to 1.0nm on K⁺ saturation and heating. Lepidocrocite is present, as well as significant amounts of amorphous materials since the cleaned clays give much clearer and prominent peaks. Extractable quantities of Si and Al are fairly similar in this profile to that from the stagnopodzol. However, the quantity of Fe_d

from bulk samples was lower than that from the podzolised brown earth, whilst Fed from the $<2\mu\text{m}$ fraction was higher. This suggests an even greater concentration of Fe in the $<2\mu\text{m}$ fraction. However, this is true of all horizons, including the surface horizon, which is not the case for the stagnopodzol E_{ag} horizon.

Unlike the stagnopodzol, the B_s horizon does not show clear differences between the upper and lower B_s in terms of the clay mineralogy. The B_{s2} horizon has a similar mineralogy to the BC horizon, dominated by hydrous mica, chlorite (stable) and vermiculite, but with larger proportions of regularly interstratified hydrous mica/vermiculite and lepidocrocite. The mineralogy of the B_{s1} is very similar to this.

The mineralogy of the surface horizon (A_h) is again similar to those below except that chlorite comprises a smaller proportion of the minerals and little lepidocrocite is present. The chlorite is, however, stable even when heated to 550°C indicating that this profile has been less intensely weathered than the stagnopodzol.

6.3.5 Minerogenic sediments from the Cefn Mawr peat core

The core taken from the peat bog at Cefn Mawr (SH908573) is described in section 6.9. Below 402cm the sediment is minerogenic, and this was sampled and treated as outlined in section 5.3 in order to study the mineralogy of its clay fraction. A sample taken at 410cm is dominated by hydrous mica and chlorite. Vermiculite is also present as seen from the ratio of 1.0/1.4nm peak heights between the Mg^{++} saturated and the K^+ saturated samples. Peaks at 1.2nm and 2.4nm suggest the presence of an interstratified mineral, vermiculite/hydrous mica. The chlorite present is stable since the 1.4nm peak is not lost on heating K^+ saturated samples to 550°C .

This data is of importance since it is possible to give a youngest age for this sediment. The base of the organic deposit (399–402cm) was dated to $6,175\pm 50$ BP (SRR-5056), and thus the minerogenic sediment below must have been deposited before this time. It is possible therefore that this material can tell us something about Hiraethog during this period in terms of the depositional environment and the clay mineralogy of the surrounding soils. However, there are many problems associated with such an interpretation. It is not possible to be certain as to the origin of the material, whether it is from eroding soil (which horizon?) or from eroding rocks or "head" deposits. It is also unlikely that no further weathering occurred after the initiation of peat development, and as such what depth of peat would be required to

isolate the minerogenic material from further weathering? These questions will be discussed in further detail in section 6.3.7.

6.3.6 Minerogenic sediment from the Llyn y Foel-frech (SH919594) sediment core

Samples were removed from the inorganic portion of this core and analysed as above. All samples had a similar mineralogy to the samples from Cefn Mawr, except for an absence of vermiculite and the presence of a hydrous mica/chlorite interstratified mineral. However, the problems associated with the interpretation of this data are very similar to those outlined above, and again will be discussed in more detail in the following section.

6.3.7 Conclusions

The results discussed here relate well to those presented by other authors (Rezk, 1975; Loveland, 1984; Chapman, 1986) for soils derived from Silurian silt- and mudstones. It is possible also to compare the different profiles, in terms of their clay mineralogy, and make inferences concerning the processes that have led to the development of such differing profile characteristics.

Anderson *et al.* (1982), studying ironpan stagnopodzols in Scotland, suggested that they were the final stage in an evolutionary sequence iron podzol \Rightarrow iron humus podzol \Rightarrow ironpan stagnopodzol. For the Hiraethog Moors Avery (1990) has suggested that ironpan stagnopodzols were preceded by brown podzolic soils. If this is the case then it is possible to look at the changes that have occurred between these two stages by comparing the clay mineralogies of the two profiles.

The B_s of the podzolised brown earth has a clay mineralogy of hydrous mica, chlorite (stable), vermiculite and regularly interstratified hydrous mica/vermiculite, and the A_h has a very similar composition, although with a smaller proportion of chlorite. The B_{s2} of the stagnopodzol is similar to this, but the B_{s1}, B_f and E_{ag} differ, both containing proportionally less chlorite but with some HIV.

Thus, if there is a sequence of brown podzolic \Rightarrow ironpan stagnopodzol this has involved the complete loss of chlorite through weathering and the production of HIV in surface mineral horizons. However, as discussed in Chapter 3, the vermiculite, and therefore the HIV, has come from the hydrous mica and not from the chlorite. This

means that this pedogenic sequence must involve weathering of vermiculite to HIV and a weathering of chlorite to noncrystalline silica and cations in solution. There is considerable evidence in the literature to suggest that these processes do occur, especially in an acidic environment such as is found in stagnopodzols (Brydon *et al.*, 1968; Kodama and Brydon, 1968; Adams *et al.*, 1971; Coen and Arnold, 1972; Bain, 1977; Adams and Kassim, 1983).

It is suggested that the absence of Fe and Al hydrous oxides in the E_{ag} enhances the weathering of chlorite and other clay minerals. Brydon and Ross (1966) studied chlorite weathering in dilute acid concentrations ($10^{-2} \Rightarrow 10^{-4}M$) such as are present in podzols. In laboratory experiments, a concentration of $10^{-2}M$ HCl produced no detectable change in the chlorite, but a pH rise did occur and chemical studies suggested that both the 2:1 layer and the interlayer were dissolving. They suggested that no further change occurred due to "Al₂O₃" and "Fe₂O₃" precipitates buffering the pH at approximately 4, and coating chlorite grains so preventing the release of Mg²⁺ ions. In podzol E_{ag} horizons, they suggested, pH is high enough to precipitate Al and Fe hydrous oxides, but chlorite is still weathered. They concluded that this was due to eluviation of these hydrous oxides to the B horizon, resulting in reduced protection from weathering in the E_{ag} and increased protection in the B_s horizon. Kodoma and Brydon (1968) came to a similar conclusion. Other workers have suggested a similar role for these materials as outlined in section 3.6.2.4, and it is suggested here also that the presence of these coatings can lead to minerals present in low concentrations being masked and so not detected in samples that have not been treated to remove such amorphous materials.

The reason for the loss of chlorite from the B_{s1} and the B_f needs, however, an alternative explanation since this horizon has similar quantities of iron to the B_{s2}. Separation of the magnetic minerals and analysis of these shows that the B_{s1} has a mineral with a 1.4nm peak. However, K⁺ saturation and heat treatment results in a loss of this peak from bulk samples and indicates that this is not chlorite but HIV. This weathering of chlorite from the B_{s1} is likely to be due to the concentration of iron in larger size fractions, so rendering it unavailable for the coating and protection of clay minerals. The reasons for this differentiation of iron are discussed further in section 6.4. The total lack of chlorite in the B_f is interesting. The clay mineralogy of the B_f is almost identical to that of the E_{ag}. The B_f has a high iron concentration, is indurated and so one would expect clay minerals present to be protected. This indicates that the ironpan has formed since the loss of chlorite from this point in the profile. Since this is the case, it is proposed that the ironpan formed in an existing

bleached E_{ag} horizon, or atleast in a zone in which some redistribution of iron had already occurred, adding weight to the theory that peat accumulation led to the development of a waterlogged E_{ag} , a reduction and loss of iron, weathering of the chlorite and then the production of an ironpan, rather than the ironpan inducing waterlogging and resulting in a build up of peat.

Thus, there is potential for the change proposed by Avery (1990) to take place, and the cause of these changes is possibly the build up of an organic-rich surface horizon leading to waterlogging of the surface. Bain (1977) showed that under conditions of increased organic matter in podzolic soils chlorite was weathered more rapidly. If this was accompanied by a waterlogging of the surface horizon of the soil leading to a dissolution of Al and Fe hydrous oxides, it is likely that the result would be the differences seen today between the brown podzolic, without a peaty surface horizon, and the stagnopodzol with a peaty horizon.

The origins and sequence of events leading to the production of the stagnohumic gley soil are more difficult to determine. It is possible that, since these soils occur in areas of very low relief, they have always been gleyed, and that peat development occurred as a result of climate change or human interference. However, it has been postulated that some of these soils were once of a brown earth type (D.A. Jenkins, pers. comm.) since in thin section studies peds have been noted with a brown interior and a gleyed rim, suggesting that the gleying has been superimposed on a pre-existing brown earth. What is certain is that they have been less intensively weathered than the stagnopodzol, which may be a reflection of their gleyed nature which will serve to reduce the through-flow of water. Thus, even though the soil lacks large quantities of Al and Fe hydrous oxides, chlorite is not weathered and lost from the surface horizon, even at pH 4.5.

However, with the surface organic layer reaching 40cm in places it is possible that these soils are no longer under the influence of weathering, as water may well be moving laterally rather than vertically through the profile. This again would result in the persistence of chlorite in all horizons since the profile would be isolated from the weathering environment. This is where the data from the sediment cores is of interest. The material at the base of the core from Cefn Mawr, which is older than $6,175 \pm 50$ years BP (SRR-5057), contains hydrous mica, chlorite (stable) and traces of vermiculite. This suggests that by the time this material was isolated from the weathering environment vermiculite had started to form in this landscape. There are

even greater amounts of vermiculite in the staghomic gley soils, which suggests that pedogenesis continued here after the isolation of the Cefn Mawr sediment.

Material analysed from the minerogenic part of the core from Llyn y Foel-frech contained hydrous mica and chlorite, but no vermiculite, suggesting that this was buried before the material from Cefn Mawr. Llyn y Foel-frech has no inflowing streams, and so it is likely that all the sediment deposited in the lake has come from the erosion of the banks; it is not aeolian in nature as can be seen from the particle size distribution data (fig 6.20). The change from a minerogenic to more organic sediment is very sharp, suggesting that erosion of the banks was initially of a mineral soil and then, as peat began to build up, of the organic deposits. This suggests that the process of weathering of hydrous mica to vermiculite, and presumably the weathering of chlorite to amorphous silica, did not begin, or increased significantly in rate, after the onset of peat development at a specific site. It is more likely that here sediments laid down in the lake would have been immediately isolated from the weathering environment and so protected, whilst at Cefn Mawr pedogenic processes would have continued for a period of time until the overlying peat was thick enough, so resulting in further changes in the mineralogy.

Traces from samples from Llyn y Foel-frech show the presence of a mineral with a basal spacing of around 1.2nm which is unaffected by any of the treatments undertaken. Sawhney (1989) suggested that this is indicative of a randomly interstratified mica-chlorite mineral, and proposed that this was fairly common in soils and sediments. It does not occur in the soil samples studied due possibly to more intense weathering that has occurred in these materials.

All this allows inferences to be made concerning the past environmental conditions and the sequence of events that have led to the formation of the soils present today over the Hiraethog Moors. To conclude, it is likely that soils were initially dominated by hydrous mica and chlorite derived from the parent material, which would have been gradually weathered. With changing conditions, due to either climatic change or human interference, organic matter began to accumulate, especially in poorly drained areas. Where peat development was rapid, isolation of the underlying sediment would also have occurred, and may have prevented further pedogenic activity.

Increased leaching and podzolisation in other areas caused the destruction of chlorite, resulting in the accumulation of amorphous materials lower down the profile, and the formation of vermiculite from hydrous mica in larger quantities, along with

interstratified minerals. In some sites, mor humus gave way to peat and surface waterlogging, reducing iron compounds, removing protective coatings and allowing further weathering of chlorite until it was completely lost from the surface mineral horizons with a subsequent development of an ironpan. Continued build up of peat at the surface may now be affecting the upper B_s, causing a removal of iron from smaller size fractions and so allowing further weathering of chlorite.

6.4 Micromorphology

6.4.1 Micromorphological descriptions and quantitative analyses

Full field descriptions of profiles are presented in Appendix IVd,e and f. The following are summaries of micromorphological descriptions of vertical and horizontal sections from each horizon: full micromorphological descriptions based on the Bullock *et al.* (1984) system can be found in Appendix IVd,e and f. All point count data are presented in Appendix IVa,b and c.

6.4.1.1 Ironpan Stagnopodzol

Figure 6.9 Point count analysis of an ironpan stagnopodzol profile (P3).

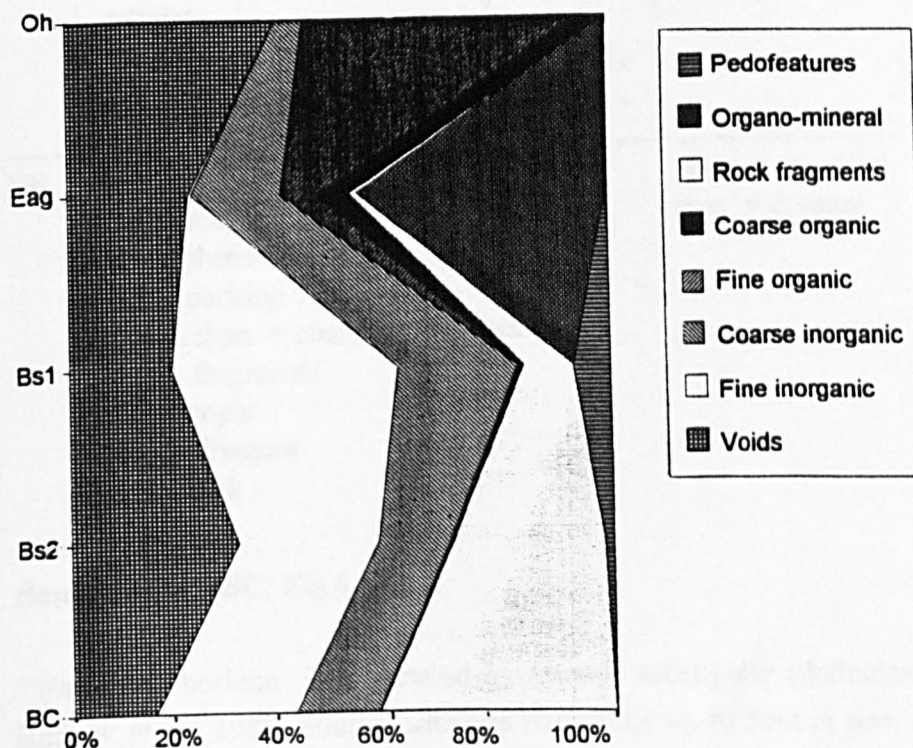


Table 6.6 Summary of the micromorphological features noted in thin sections

Feature		Ironpan stagnopodzol soil					Stagnohumic gley				Brown podzolic soil				
		Oh	Eag	Bf	Bs1	Bs2	BC	Oh	Eag	Bg	BCg	Ah	Bs1	Bs2	BC
Peds	subangular bl.	+	+	+	+	+	+	+	+	+			+	+	+
	sph. crumbs	+	+			+		+	+				+	+	+
	angular bl.			+						+	+		+	+	+
Voids	complex pack.	+	+		+	+	+	+	+	+	+	+	+	+	+
	vughs	+	+	+		+	+	+	+	+	+			+	+
	planar			+						+	+		+		
	vesicles				+	+			+	+					
	chamb./chan.					+				+					
Stone frag.	fresh	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	pellicular alt.			+	+	+	+						+	+	
	cryptic		+						+	+	+				
Coarse organic	i. tissue	+								+	+				+
	b. tissue								+		+				
	i. organ	+										+			
	b. organ	+	+	+	+	+	+	+	+	+		+		+	
	blk. organ	+							+	+			+		
	blk. tissue	+	+		+	+	+	+	+	+			+	+	
Fine organic	i. red/brown	+	+	+	+	+	+	+	+	+	+	+	+	+	
	b. yellow	+						+	+						
	pigmentation		+						+				+		
	blk.	+			+	+	+	+					+	+	+
B-fabric	stipple spec.		+	+	+	+	+		+	+			+	+	+
	mosaic spec.										+				
Pedofeatures	excrement		+	+					+				+		+
	hypo-coat.				+				+	+	+				
	typic-coat.		+		+				+	+	+				
	quasi-coat.									+	+				
	cutans					+	+			+	+			+	+
	nodules		+	+	+	+	+						+	+	+

NB. + = presence

bl. = blocky

sph = spheroidal

pack = packing

chamb./chan. = chambers/channels

Frag. = fragments

i. = isotropic

b. = birefringent

blk. = black

spec. = speckled

coat. = coating

Basal horizon (BC; Fig 6.10a)

This stoney horizon is dominated by smooth subangular (definitions in Fig. 31 in Bullock *et al.*, 1985) Silurian siltstone fragments, up to 5cm in size, making up over 50% of sections. They are occasionally cracked and exhibit pellicular alteration which

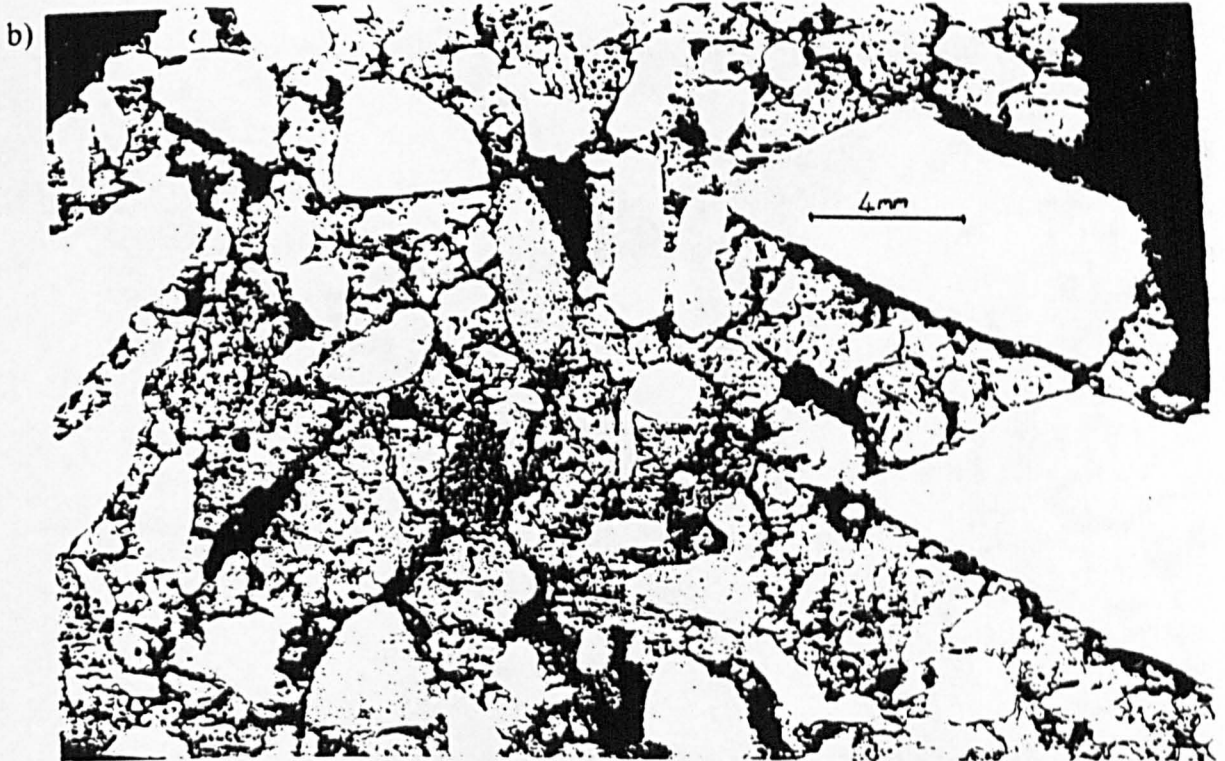
usually comprises only 20% of a stone. Voids are mainly compound packing voids, up to 1mm in width, with an ultrafine to fine angular blocky and ultrafine spheroidal crumb structure between the siltstone fragments, although porosity is only 15-20% (pores <1mm diameter). The material making up peds is almost entirely inorganic with only rare organic materials noted, usually small (<500µm) roots in varying stages of decay. The coarse component is dominantly subangular quartz grains with mica and chlorite, whilst the fine fraction is inorganic, red-brown and exhibits little aggregate birefringence; where it does it gives a stipple-speckled b-fabric. Pedofeatures comprise <1% of sections and are dominantly textural except in the region where the BC merges with the lower B_s; here strong to moderately impregnated red-brown nodules occur with red-orange interference colours. Textural pedofeatures are comprised of rare impure or limpid clay void coatings exhibiting aggregate extinction, which are red-brown stained; similar features occur embedded in the matrix, occasionally with truncated edges. They are usually banded with darker bands of similar material, and with coarser material to form a sequence of clay and silt/sand bands. Many ped surfaces are coated with thin (10µm) pale yellow birefringent argillans, which coat both ped and coarser argillan surfaces. These are noted on argillan surfaces, but not within argillans.

B_s horizon (Figs 6.10b,c and d)

Micromorphological characteristics differ between the upper and lower sections of this horizon. Subangular siltstone fragments make up around 50% of the lower B_s (B_{s2}), showing no obvious preferred orientation and occasionally exhibiting cracks and/or pellicular alteration, up to 1mm thick and comprising up to 60% of a stone. Porosity is around 30% with peds being either ultrafine to very-fine subangular blocks or ultrafine spheroidal crumbs, occasionally the one merging into the other. Compound packing voids dominate with some vughs and channels occurring within peds. Mineral and organic components are very similar in type and quantity to the horizon below. Pedofeatures, which make up ≈3%, are dominated by nodules, either moderately to strongly impregnated with orange-red interference colours or pure with orange-red interference colours and aggregate extinction. Pale yellow birefringent coatings up to 10µm thick occur around some of the spheroidal peds. Black organic deposits embedded in the matrix are identified as charcoal; fragments removed from the soil were identified as *Alnus* (Dr P. Denne, pers. comm., 1995).

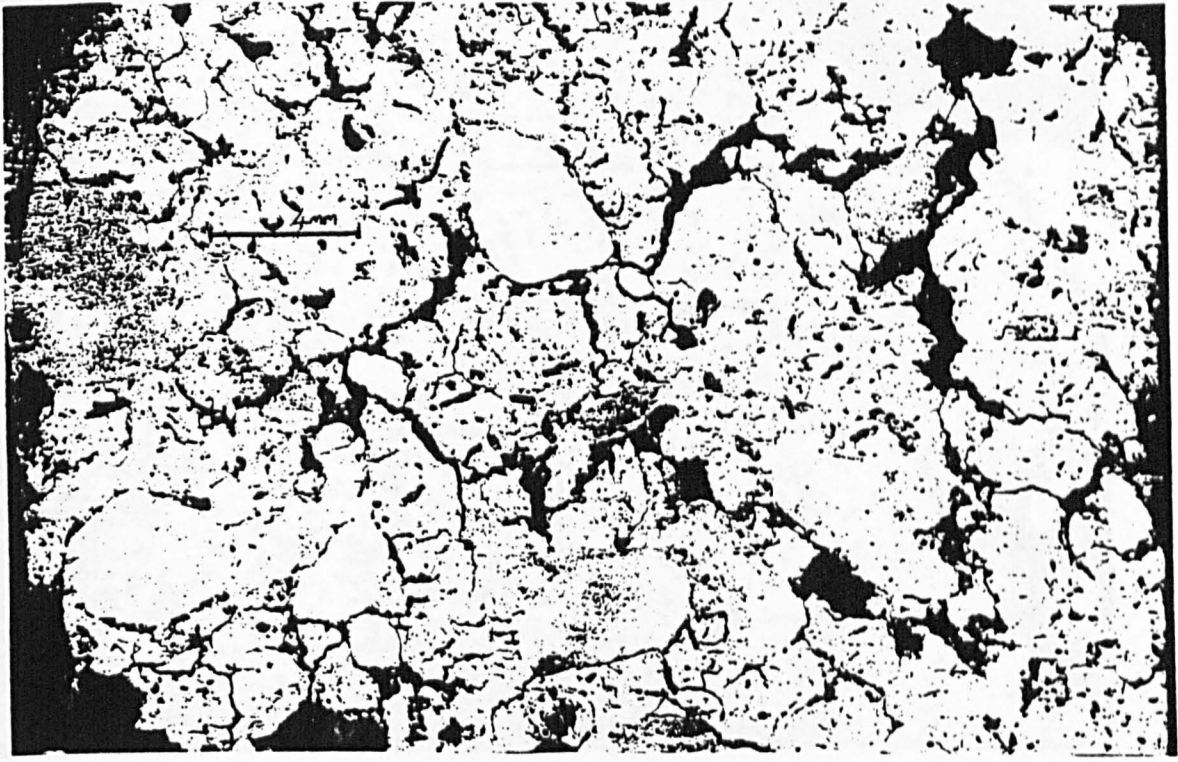
Figure 6.10 Structure of an ironpan stagnopodzsol seen in thin section; a) BC
b)B_{s2} c)B_{s1} d)B_f e)E_{ag} f)O_h

All sections vertically orientated ———>

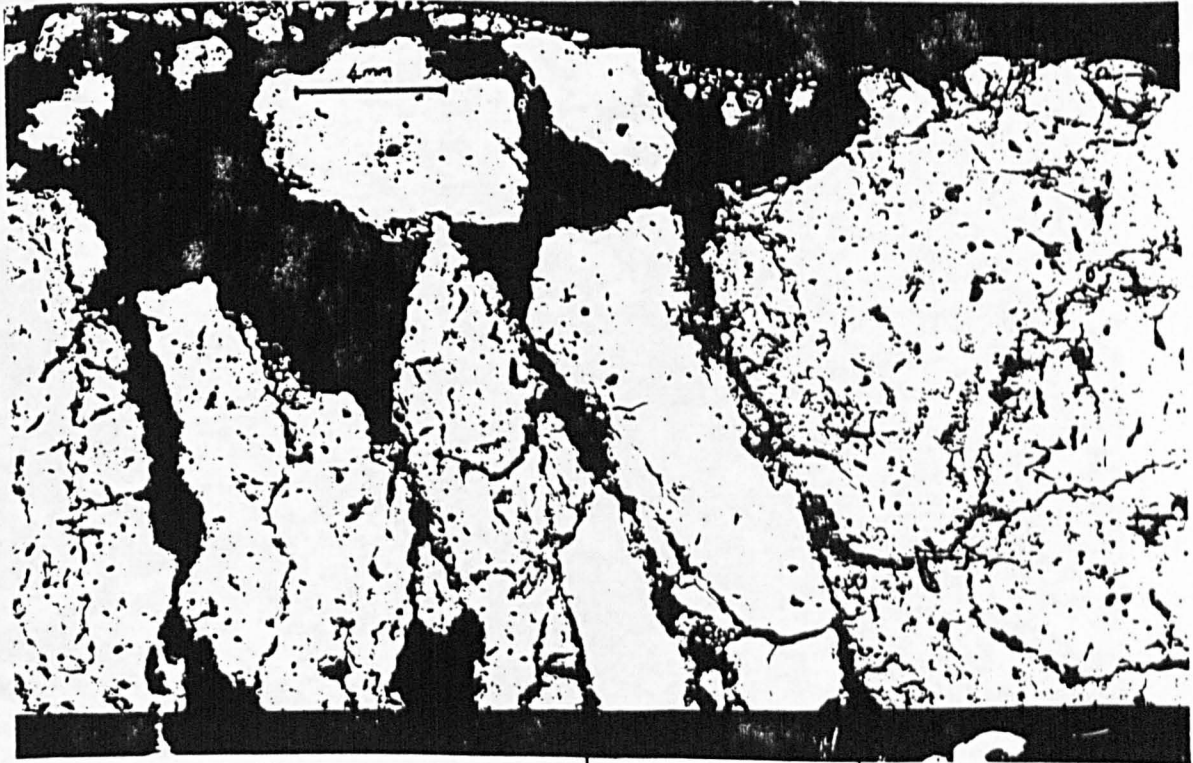




c)

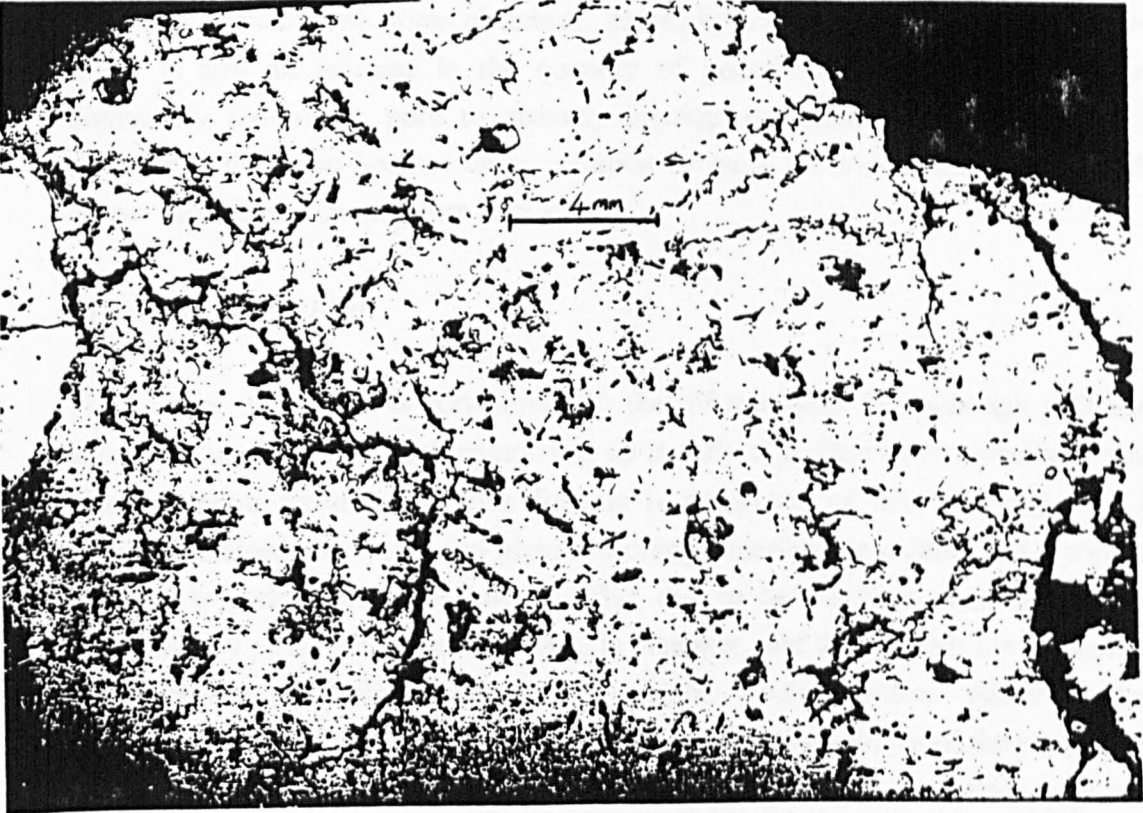


d)





e)



f)



The upper B_s (B_{s1}) has a similar composition in terms of its inorganic and organic components, but a different microstructure. Peds are now composed only of ultrafine to very fine subangular blocks and porosity is reduced to <20% as compound packing voids and vesicles with some chambers, especially towards the top of the horizon. There is also an increase in the quantity of pedofeatures to 5-8%. These are dominantly red-brown, pure to strongly impregnated nodules up to 1500µm in diameter, which also become more common towards the top of the B_s. The pale yellow birefringent coatings are now absent.

Bf horizon (Fig 6.10d)

The mineral component is very similar to that of the upper B_s, although pellicular alterations up to 300µm thick comprising up to 40% of a siltstone fragment are now more common features. The fine fraction is composed of silts and clays but is uniformly stained red-brown and gives red-orange interference colours and a stipple-speckled b-fabric. Porosity is low (5-10%), due to the horizons cemented nature, dominated by planar voids, up to 600µm in diameter, and vughs. Peds are comprised of ultrafine to very fine subangular to angular blocks. Coarse organic matter, composed of root residues, is mainly restricted to the upper surface of the pan, where the roots are often deformed (*ie.* not circular). Within the pan is noted orange-red, usually isotropic, dense complete or incomplete void infillings, up to 700µm thick, with very good contrast with surrounding material. These exhibit frequent planar voids (cracks) and are thought to be colloidal organic matter, *ie.* organic fine fraction.

Eag horizon (Fig 6.10e)

The quantity of identifiable rock fragments is substantially less than in lower horizons. The fine fraction is composed of silt and clay with a stipple-speckled b-fabric, although much is stained brown. Porosity is slightly higher than that of the upper B_s (\approx 25%), mainly as compound packing voids or vughs, the latter of which also occur as intra-aggregate voids. Peds are either ultrafine subangular blocks or ultrafine spheroidal granules. Where stained brown porosity is higher, where paler in colour porosity is lower giving a more vughy micro-structure. The coarse organic fraction is composed of organ and tissue residues which are restricted to void spaces. The fine organic fraction occurs as yellow isotropic dense incomplete void infillings or red-brown isotropic typic void coatings, the latter often being broken and disjointed. The brown pigmentation of some areas is thought to be due to fine organic matter.

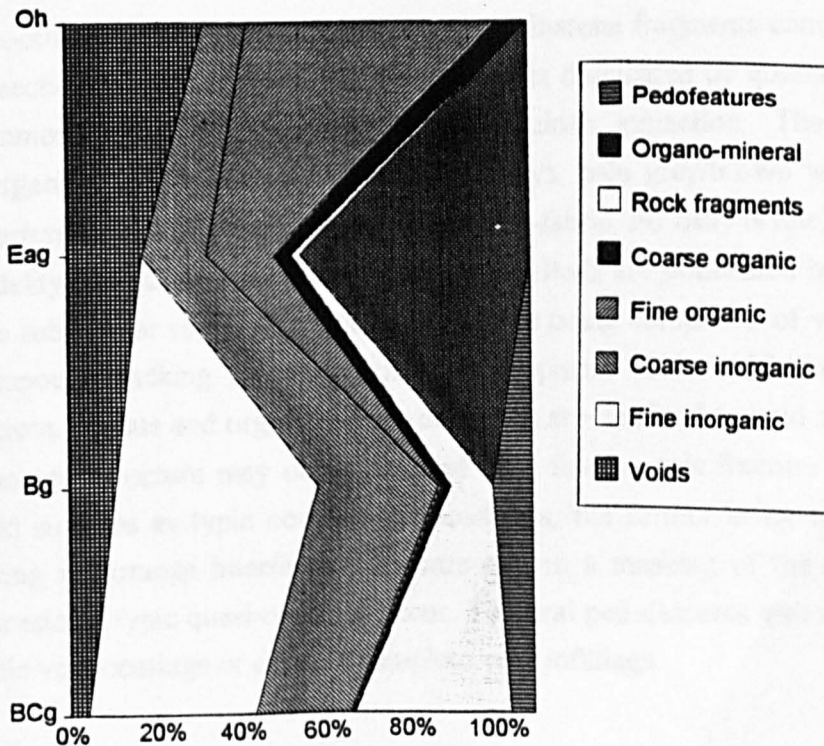
Weakly impregnated nodules occur, as well as regions of mammilated excrement pedofeatures up to 250µm in diameter; the latter show a clustered distribution and are occasionally coalesced into porous deposits.

Oh horizon (fig. 6.10f)

This horizon is dominated by voids and organic fine material. Porosity is 30-40% with coarse inorganic material and rock fragments comprising only around 7% with a random distribution and orientation pattern. Voids are dominated by compound packing voids with some intra-aggregate vughs. Peds are ultrafine to very fine subangular blocks and ultrafine spheroidal crumbs. The coarse organic fraction is composed of randomly distributed organ and tissue residues, usually associated with voids. Fine organic matter is found in several forms: (a) red-brown with yellow-orange interference colours; (b) black; (c) pale brown and isotropic; (d) yellow and exhibiting aggregate extinction. No pedofeatures, except possible faunal excrements produced by Oribatid mites (spheroidal crumbs), occur in this horizon. The matrix shows no U V auto-fluorescence, although occasional auto-UV-fluorescent features are noted, often kidney shaped and presumably relating to organisms which have been present in this horizon.

6.4.1.2 Stagnohumic gley soil

Figure 6.11 Point count analysis of a stagnohumic gley profile (P2).



Basal horizon (BC_g; Fig 6.12a)

This horizon is dominated by the inorganic fraction. Smooth subrounded siltstone fragments make up 20-30% of sections, and are often internally divided by planar voids, some of which contain argillans. No pellicular alteration is noted since all fragments are dark to very pale grey in colour *ie.* lacking imposed pigmentation. Quartz grains dominate the remainder of the coarse fraction, along with mica and quartz and heavy minerals. The fine fraction is composed of silts and clays, pale grey with white to grey interference colours giving a mosaic-speckled b-fabric. Porosity is low (<10%) and pedality is very weakly developed. Voids are dominated by compound packing voids and vughs. Organic matter levels are very low (<1%). The coarse fraction is dominated by tissue and organ residues which are always associated with voids. Several organic structures, exhibiting differing levels of birefringence, are often present within one void. The fine fraction occurs as red-brown isotropic void coatings. Pedofeatures comprise 2% of sections, and occur as either amorphous/cryptocrystalline or textural pedofeatures. The former are dominated by typic coatings or hypocoatings, coatings being isotropic, hypocoatings giving red/orange interference colours. Textural pedofeatures are composed of dense incomplete void infillings of pale grey, dusty or impure clay with occasional silt-sized inclusions, with good to poor contrast with the surrounding material. They also occur embedded in the matrix with very low contrast and are often banded.

B_g horizon (fig 6.12b)

Smooth rounded, frequently cracked, grey siltstone fragments comprise around 10% of sections. The rest of the coarse fraction is dominated by quartz grains which are commonly polycrystalline or exhibit undulose extinction. The fine fraction is inorganic, being comprised of silts and clays, pale grey/brown with white to grey interference colours and a stipple-speckled b-fabric. Porosity is low, around 10%, and pedality is weakly to moderately developed. Peds are dominated by ultrafine to very fine subangular to angular blocks with voids being comprised of vesicles, vughs and compound packing voids with occasional planar voids, exhibiting a zig-zag crack pattern. Tissue and organ residues occur but are confined to void spaces where more than one structure may occupy a void. The fine organic fraction is associated with void surfaces as typic coatings/hypocoatings, the former being isotropic, the latter giving red-orange interference colours due to a masking of the underlying matrix. Occasional typic quasi-coatings occur. Textural pedofeatures also occur as dusty clay typic void coatings or dense incomplete void infillings.

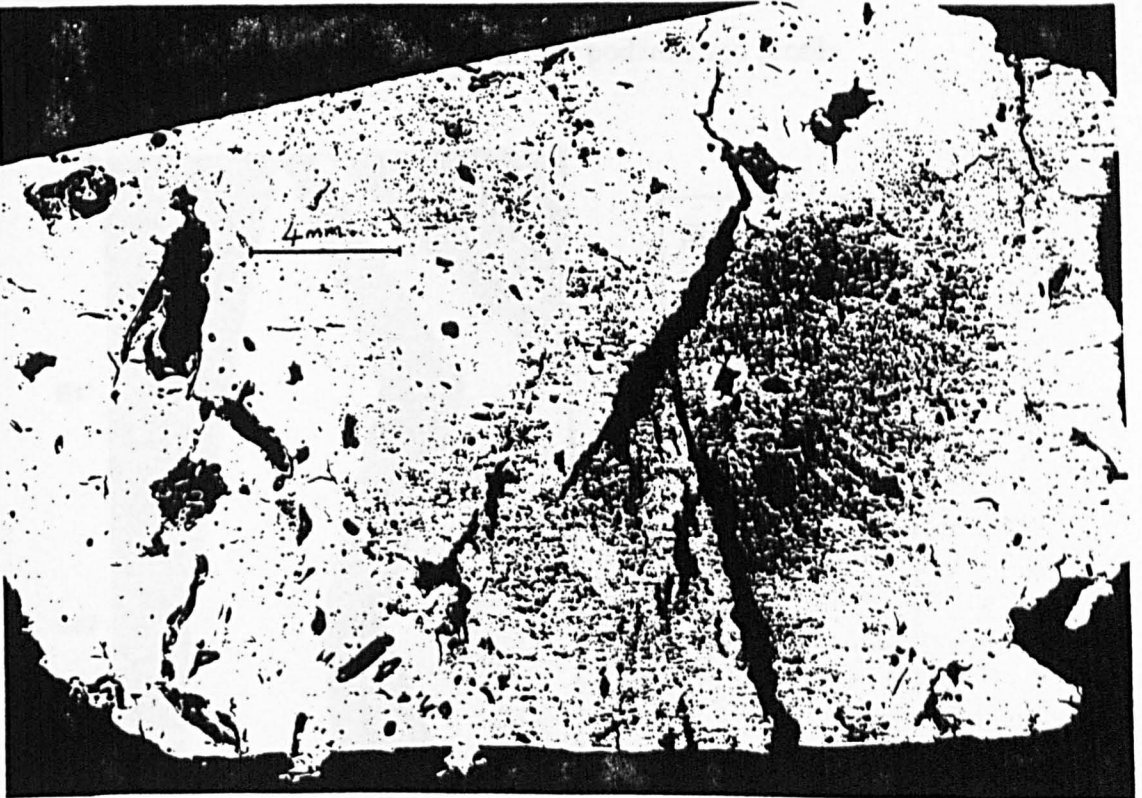
Figure 6.12 Structure of a stagnohumic gley soil seen in thin section; a) BC_g b)B_g



a)



b)



Eag horizon

This horizon is very similar to that of the stagnopodzol. "Recognisable" (*ie.* not merging with the general soil fabric) siltstone fragments are infrequent and pedality is only moderately developed, especially in regions more heavily influenced by organic pigmentation. Peds are dominantly very fine subangular blocks with occasional accumulations of ultrafine spheroidal crumb peds, often within void spaces. Voids are mainly compound packing voids, becoming more vughy where pigmentation by fine organic matter is less. Tissue and organ residues are commonly found within voids, and the fine organic fraction is dominated by organic pigmentation of the groundmass. Red-brown void surface coatings or infillings occur which are isotropic, and pale yellow laminated deposits, which exhibit weak UV auto-fluorescence, also occur.

Oh horizon

This is very similar in structure and composition to that present in the stagnopodzol.

6.4.1.3 Typical brown podzolic soil

Figure 6.13 Point count analysis of a brown podzolic soil profile.

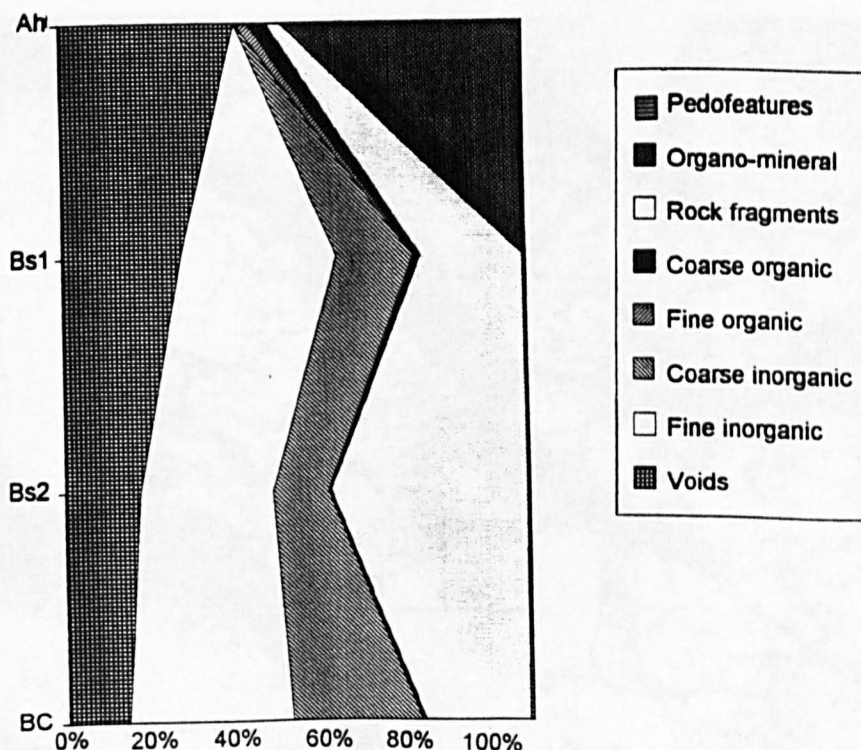
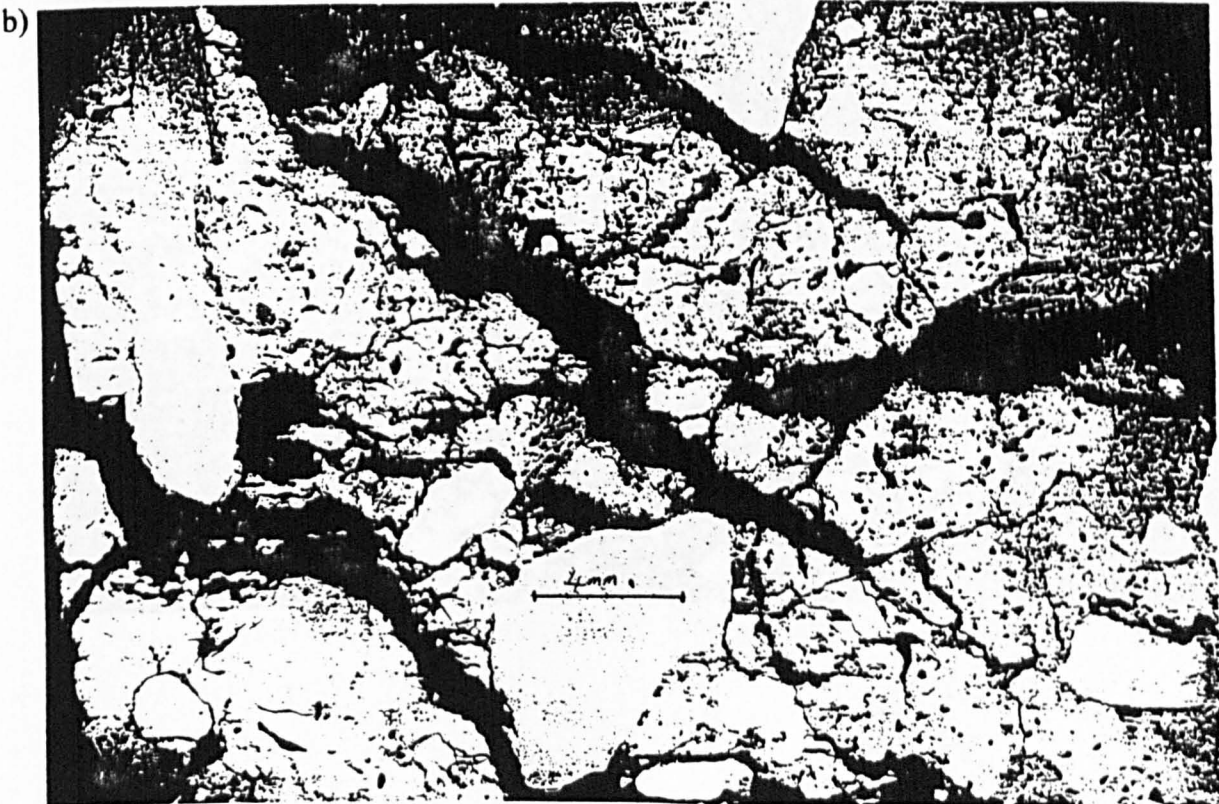
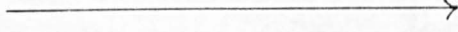
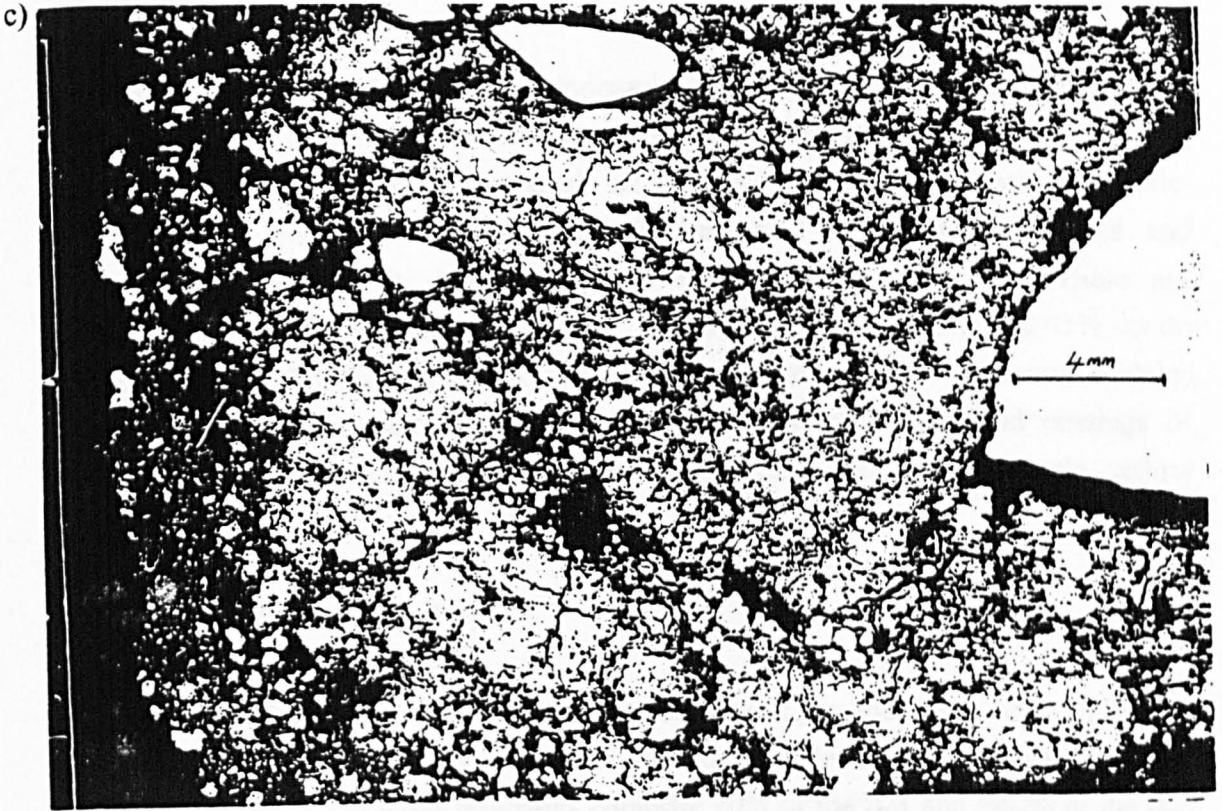


Figure 6.14 Structure of a brown podzolic soil seen in thin section: a) B_{s2} b) B_{s1}
c) A_h d) Detail of an ovoid feature in the B_{s1} (vertical section)





BC horizon

This horizon is dominated by the inorganic fraction. Smooth sub-angular siltstone fragments, up to 3cm in size, comprise over 50%, often with planar cracks running through them. The remainder is sand, silt and clay with a stipple-speckled b-fabric. Porosity is $\approx 20\%$ with interstone peds dominated by subangular blocks and spheroidal crumbs, the latter often showing signs of coalescence. These are surrounded by compound packing voids. The organic fraction comprises $<1\%$, as do pedofeatures. The latter occur as typic moderately impregnated red-brown nodules with red-orange interference colours, and as impure clay typic void coatings or infillings, red-brown with yellow-orange interference colours. No pale yellow coatings were noted.

B_s horizon (fig 6.14a and b)

The micromorphological differences between the upper and lower sections of this horizon are less well marked than in the stagnopodzol. Smooth subrounded to subangular brown siltstone fragments comprise 20% of the B_{s1} and $>40\%$ of the B_{s2} and show cracking and/or pellicular alteration up to 1mm in width. The rest of the coarse fraction is dominated by quartz grains which may exhibit polycrystallinity or undulose extinction along with mica and chlorite grains. Porosity is higher in the B_{s1} (25.4% *cf* 16.2%), but in both portions peds are composed of ultrafine to very fine subangular to angular blocks and ultrafine spheroidal crumbs, with voids being dominantly compound packing voids. Both have little organic matter. The fine fraction is dominated by black material (charcoal) embedded in the groundmass whilst the coarse fraction, which is more abundant in the upper part, is composed of black tissue residues and birefringent organ residues, the latter always occurring within void spaces and probably representing root sections. Red-brown nodules, strongly to moderately impregnated, occur in both with a random distribution. Textural pedofeatures, however, are only found in the lower B_s and are composed of dusty or impure clay typic void coatings or dense complete void infillings, red-brown with yellow-orange interference colours. No pale yellow coatings noted.

An ovoid feature as noted in the profile description in Appendix IVe, 8cm at its widest point in diameter, in the upper B_s has a structure and composition very similar to the A_h, except that peds are larger and have a vughy structure in terms of intra-aggregate voids (fig 6.14d).

***A_h* horizon (fig 6.14c)**

Smooth sub-angular siltstone fragments, up to 5mm in diameter, occur but only comprise around 5% of sections. Pedality is moderately to strongly developed with peds being dominated by ultrafine to very fine angular blocks and ultrafine spheroidal granules which merge into the larger units. Porosity is high, around 40%, being dominated by compound packing voids. Organic coarse material is dominated by pale yellow birefringent organ residues, always associated with voids. The fine fraction is dominated by a dark, isotropic material mixed in with the inorganic fraction. Other forms include pale yellow isotropic deposits and orange-red dense incomplete void infillings which exhibit aggregate extinction.

6.4.2 Interpretations and discussion

6.4.2.1 Basal horizons

The stagnopodzol and brown podzolic soil are considered to have formed on "head" deposits (see section 6.2 on fabric analysis), and this is reflected in the micromorphology of their lowest horizons. The point count data of these indicates that they are dominated by angular rock fragments, in this case Silurian silt- and mudstones, suggesting a local origin for the material comprising the head deposit. Porosity is generally low and the soil material between stones is dominantly inorganic with the little organic material present generally restricted to void spaces. The point count data matches well that for percentage stone content presented in section 6.2.

Micromorphologically, however, the basal horizons of the two podzols and the gley are very different. Rock fragments in the stagnogley are usually pale, often lacking clear boundaries with the surrounding material, whilst those in the podzols are dominantly red-brown and very easily distinguished from the soil matrix. This reflects the waterlogged nature of the BC_g horizon, suggesting that iron has been reduced and that rock fragments, under such conditions, have become completely rehydrated. There are, however, occasional fragments which retain some brown colouration at their core which may be a result of their having previously existed in an aerated environment which has subsequently become anaerobic. This relates to the "stone rim bleaching" noted by Crampton (1963) and Macphail *et al.* (1987) in gleyed surface horizons of peaty-gleyed podzols, which they took to indicate the previously aerated nature of the soils. It is also possible that the lower percentage of rock fragments

recorded for the BC_g, as compared to the % stone content figures by point counting, reflects to a certain degree the difficulty in distinguishing completely altered rock fragments from a massive material of similar texture and colour.

However, fragments in all the soils studied exhibited planar cracking voids. Some such voids were noted with clay deposits on their surfaces indicating that they were formed prior to clay translocation, possibly as a result of periglacial activity. This is based on the assumption that, as Catt (1989) suggested, argillans in soils of N.W. Europe are relict early Holocene features since the soils in which they occur are now too acidic for clay translocation. This is reinforced by the presence of a coalesced spongy fabric within planar cracks in fragments of rock in the lower B_g horizon of the stagnopodzol. If this fabric relates to an earlier "brown earth" phase of soil development, the cracks must precede this and would therefore most probably relate to periglacial processes. Other freeze/thaw features are seen in exposed sections around the margins of the reservoir, including shattered rocks and cryoturbation features such as stone festoons. This would confirm the results which suggest the parent material is a periglacial "head" deposit. Cracks and pellicles occur in the same stone fragments, but no sequential inferences can be drawn from such features since in all cases observed the cracks do not cut through the pellicles into unaltered rock, and no crack has an associated pellicle, and therefore no sequence of events can be inferred from these features.

Porosity and microstructure also differ between basal horizons of the podzolic and gley soils. Porosity is lowest in the stagnogley due to a weakly developed pedality giving a fairly massive structure, with voids as vughs or compound packing voids and the inorganic fraction dominated by silts and clays. It is likely that this structure developed due to a disaggregation of rock fragments into their prime particles which, without the influence of biological activity or structural stabilisers such as Fe and Al hydrous oxides, would produce a massive structure. This process could have also occurred if the soil had initially been a brown earth type soil. As biological mixing was excluded and iron lost, any existing structural units may have collapsed into close packing of their constituent particles giving a massive structure. This is suggested since some peds have a brown core with a grey surround (D.A. Jenkins, pers. comm., 1994) which may represent such a past pedogenic phase. Porosity in the podzols is greater and pedality more developed giving a subangular to angular blocky structure with compound packing voids. The soil is red-brown coloured indicating an oxidised state and the presence of stabilising Fe hydrous oxides which prevents the collapse of

pedes to the prime particles, silts and clays, as suggested by Deshpande *et al.* (1964).

Both textural and cryptocrystalline pedofeatures occur in the basal horizons of all the profiles studied, but again there are differences. Cryptocrystalline pedofeatures in the stagnohumic gley occur as typic- or hypocoatings. Typic coatings are red-brown and isotropic, suggesting they may be well decomposed root residues whilst hypocoatings give red-orange interference colours, indicating a masking of the birefringence of silt and clay particles, possibly by iron, Fe^{2+} becoming oxidised in the better aerated zones around voids. This does not occur around all voids which may be due to a segregation of the low amounts of iron in the profile, most of it having been lost in drainage waters. Cryptocrystalline pedofeatures in the podzols are dominantly strong to moderately impregnated nodules, all of which give red-brown interference colours indicating a masking of silt and clay particle birefringence properties, again possibly by iron.

Textural pedofeatures occur as void coatings or infillings of dusty or impure clay in all the profiles, although in the stagnogley these generally have a pale grey colour, unless they occur as void coatings when they may be stained red-brown by organic matter and/or iron, whilst in the podzols they are dominantly red-brown with yellow-orange interference colours, again reflecting the reduced nature of the gley soil. In all profiles fragments of such infillings and coatings can occur embedded in the matrix with truncated edges suggesting that, since their deposition there has been a phase of soil disturbance. However, it is possible that some such features in the stagnogley simply represent remnants of silt- and mudstones, completely altered, the banding simply representing that present in the original rocks (fig 6.15a and b). However, many cutans occur undisturbed suggesting that since this period of soil development, the BC has experienced minimal disturbance, which may be explained by a lack of bioturbation and the accumulation of large quantities of stabilising Fe^{3+} compounds.

Nevertheless, there are differences between the stagnopodzol and brown podzolic soils. In the stagnopodzol, thin pale yellow birefringent argillans occur around pedes and on other argillan surfaces, which do not occur in the brown podzolic soil (Fig 6.15c and d). EDXRA results (Appendix Va, b and c) show that this is some form of mica (*ie.* Si, Al, K) and not an amorphous material (Al, Si, Fe); it is also birefringent. This difference clearly relates to the different processes which have occurred in these two soils, possibly to the increased weathering in the stagnopodzol surface mineral horizon resulting in the release of very fine mica which could be moved in suspension and be redeposited deeper in the profile. In the brown podzolic soil many void

surfaces carry cutans, some relatively thin ($\approx 10\mu\text{m}$), but red-brown in colour (PPL). These therefore differ from the pale birefringent argillans seen in the stagnopodzol. The fact that the thin argillans in the brown podzolic soil are red-brown suggests that the pale argillans in the stagnopodzol are formed from clay material low in iron form an established E_{ag} horizon, or have been reduced subsequent to deposition, although this latter is unlikely since no other features in this horizon show signs of reduction.

In analysing some pale yellow isotropic coatings a problem was highlighted. Some seemed to relate micromorphologically to the material first described by Claydon (1970), but on EDXRA analysis (Appendix Ve) were found to simply represent cracks at void surfaces in the impregnated block which had become filled with the resin used to attach the block to the glass slide. This highlights the importance of using several approaches to characterise features first noted in thin sections.

This does, however, raise the question of why the features noted by Claydon (1970) and described as allophanic by Farmer *et al.* (1985) have not been observed in these profiles. Claydon (1970) described them as "plasma", but does not suggest they are allophanic and does not comment on their birefringence. It may therefore be that the "linking plasma" noted by Claydon (1970) is in fact fine argillaceous material. The material studied by Farmer *et al.* (1985) was a cemented B horizon from a sandy podzol, and they described such deposits as isotropic or weakly anisotropic, yellow and commonly auto UV fluorescent; those from Hiraethog are birefringent and not UV auto-fluorescent. One small area, noted in figure 6.17c, did give an EDXRA line scan spectrum of dominantly Si without K (Appendix Vd) and was isotropic. However, spot analyses failed to duplicate this result and therefore it is not possible to confirm that this is allophanic material.

Farmer *et al.* (1985) did, however, suggest that, although allophane with an imogolite-like structure (proto-imogolite allophane) has been shown to be present in amounts up to 18% of the $<2\text{mm}$ soil in the B_s horizon of podzols, this material has not generally been recognised in thin sections. A material similar to this is noted in some voids in the cemented B_f horizon of these soils, but on analysis it was found to contain only Fe ($\pm\text{C}$; Appendix VI and figure 6.15n and o), and therefore, in the case of stagnopodzols and brown podzolic soils from the Hiraethog Moors, no allophanic material could be identified by micromorphological techniques.

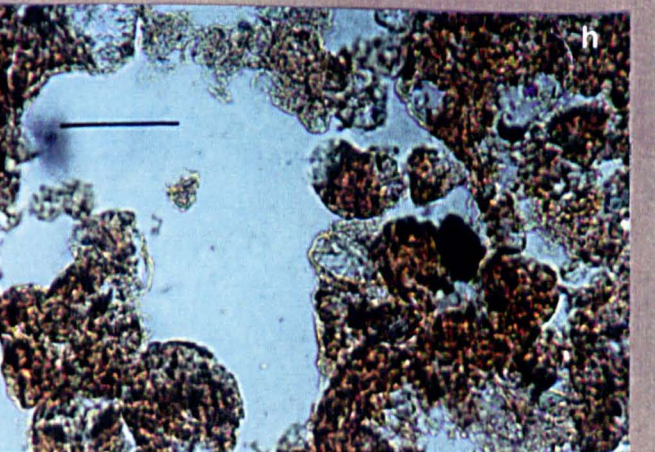
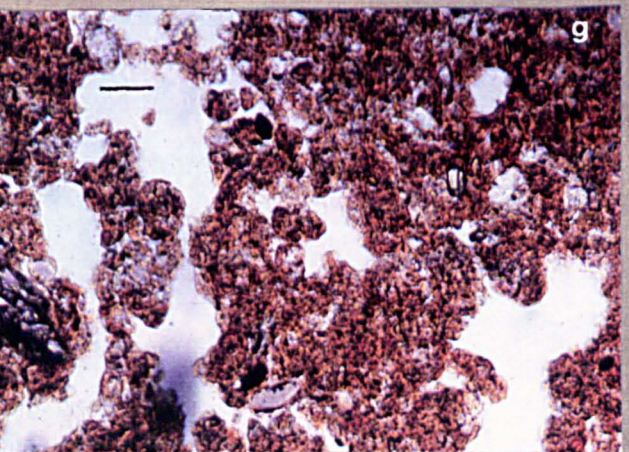
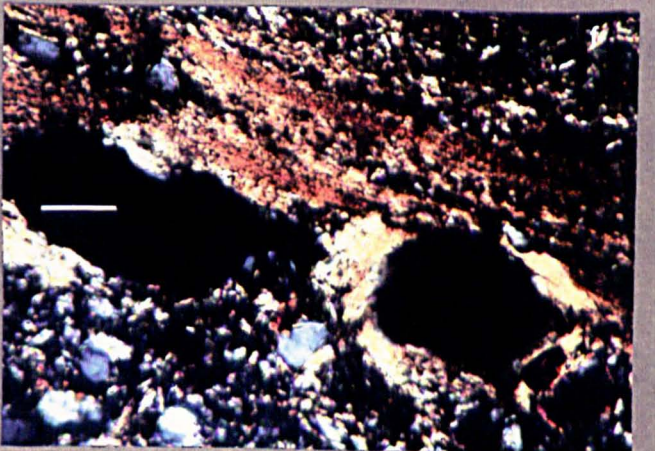
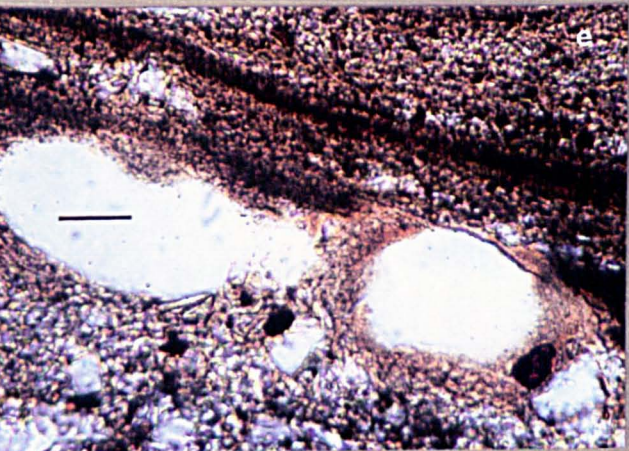
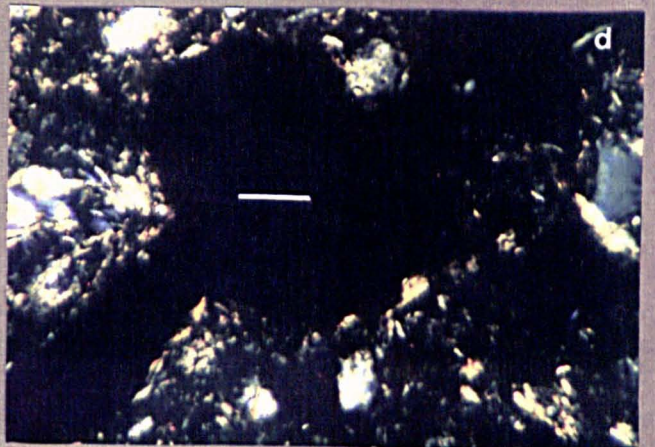
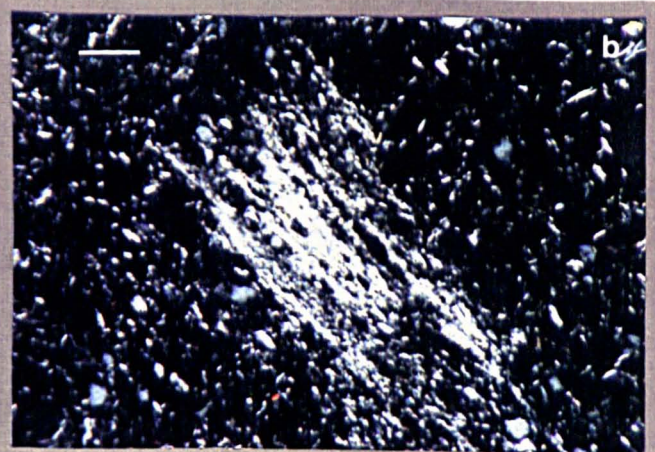
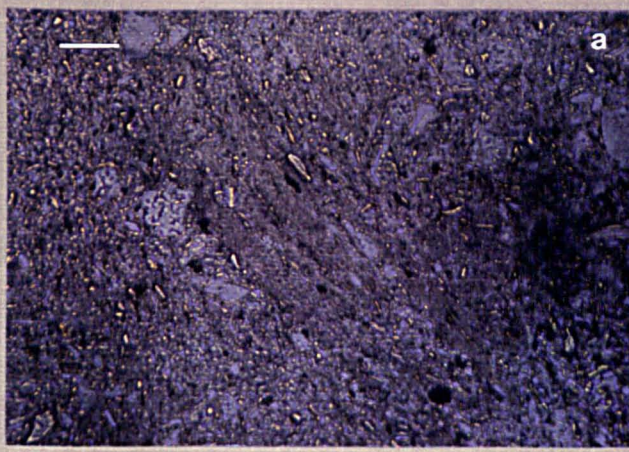


Figure 6.15a-h a) Remnant of a siltstone fragment in the BC_g of the stagnohumic gley (bar=100μm) b) a) in XPL. c) Thin, yellow, slightly birefringent argillan coating a void surface in the basal horizon of the ironpan stagnopodzsol (bar=20μm). d) c) in XPL e) Voids superimposed on an existing argillan in the basal horizon of the ironpan stagnopodzsol around which a later phase of clay deposition has occurred. Note the dark banding of the main argillan (bar=20μm). f) e) in XPL g) "Spongy" fabric of the Bs₂ in the ironpan stagnopodzsol (bar=50μm). h) Detail of g) showing fabric and pale yellow ped coatings.

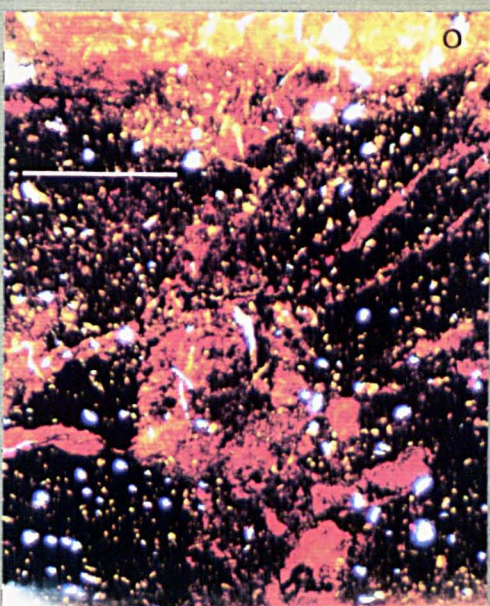
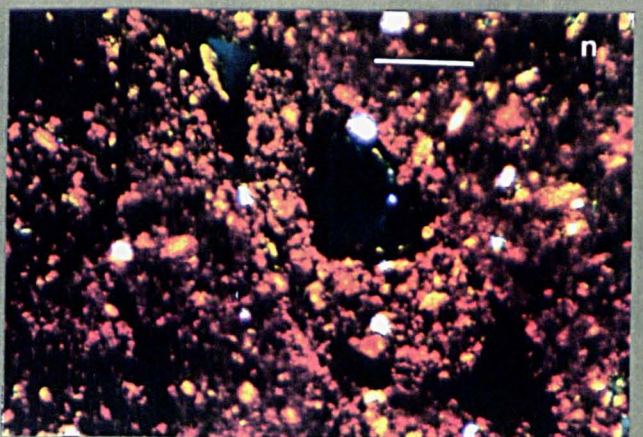
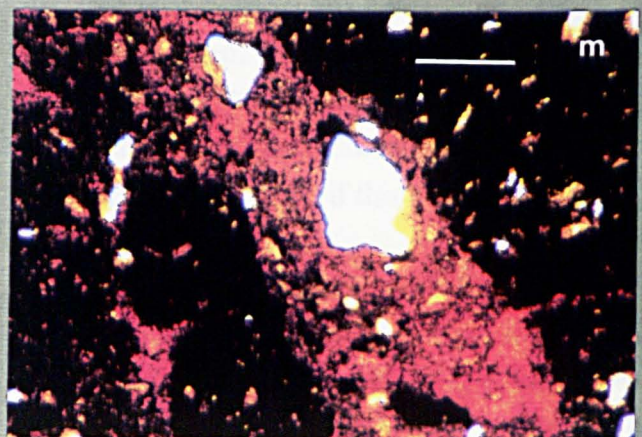
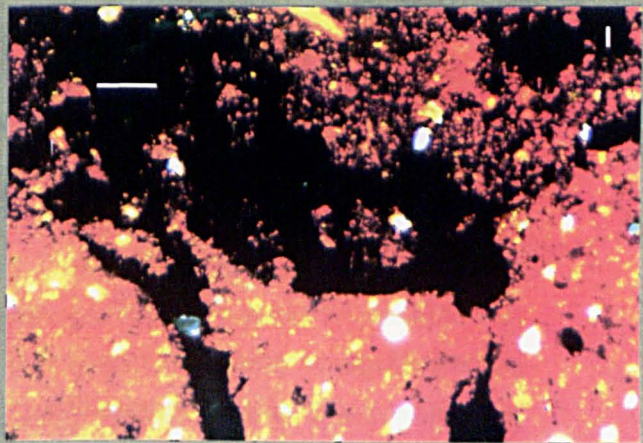
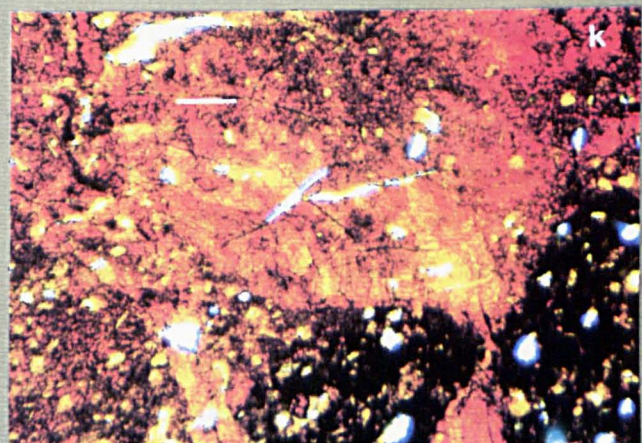
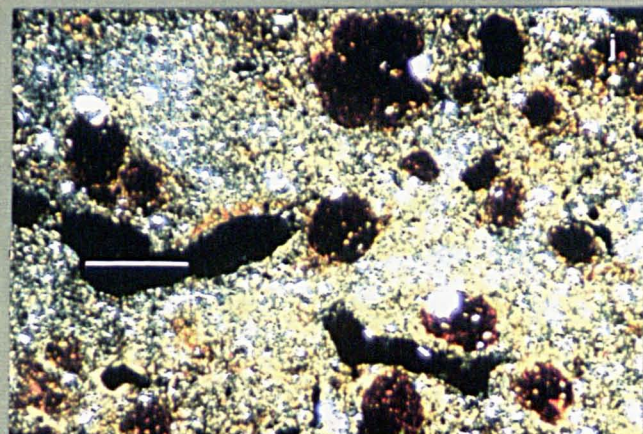
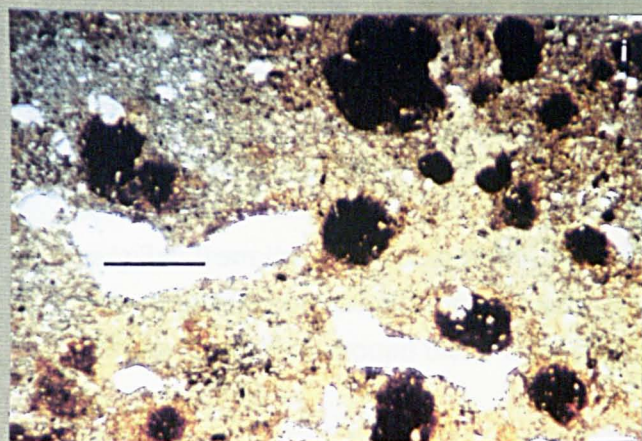


Figure 6.15i-o i) Fabric of the B_{S1} of the ironpan stagnopodzol showing the massive structure, pale colour and nodules (bar=500µm). j) i) in XPL. k) Red-brown, cracked, isotropic void infillings in the B_f of the ironpan stagnopodzol (bar=50µm). l) k) in XPL. m) Void at base of ironpan with typical coatings of red-brown (isotropic) and black material (bar=50µm). n) m) in XPL. o) B_f (ironpan) horizon of the ironpan stagnopodzol (bar=500µm).

In some cases argillans are banded, up to 10 times, with alternating accumulations of silt/fine sand sized material and clay, suggesting phases of translocation. One such argillan from the stagnopodzol BC horizon shows evidence of a second generation of clay translocation and deposition where the argillan contains voids with another phase of clay deposition around these voids (fig 6.15e and f).

EDXRA was carried out on a similar feature (Appendix Vf,g and h), and this shows that the dark banding relates to higher concentrations of iron in the clay deposit. This feature also showed a distinct increase in particle size towards the centre of the deposit. Sharp peaks in Si corresponding with low levels of K and Al suggest that some of this coarser material, which is not optically resolvable, is quartz. The associated voids cutting into it, one of which has further clay deposits, represent a different and later phase of clay translocation. From the EDXRA results this second phase can be seen to have higher Si and K peaks and lower Fe peaks (Appendix Vh), whilst having similar amounts of Al. The lower amounts of Fe may be significant and there are several possible explanations which could account for this. It is possible that the clay material has come from a region lower in Fe quantities, ie. more weathered and leached, or that it has come from a less intensely weathered area where less Fe has been liberated. It is also possible that since deposition the material has been reduced, although this is unlikely since none of the other clay deposits are affected which might be expected if this had been the cause.

Some cutans, as exemplified by the one described above, show a gradual grading from pure clay to dusty clay and silt with less orientation of the latter (*ie.* less aggregate birefringence). It is possible that this and the silt/clay banding correspond to features noted by Scaife and Macphail (1983) and Romans and Robertson (1983) which they suggested were caused by an intensification in human activity which led to a reduced vegetation cover and increased breakdown of surface aggregates, reduction in stabilising organic matter content and increased mobilisation of clays, including an increase in the coarser component that was moved.

6.4.2.2 B horizons

Micromorphological differences occur throughout the remainder of the profiles. The B_g horizon of the stagnogley has less stone fragments than the BC_g horizon and a slightly more developed structure, giving subangular to angular blocks with vesicles, vughs and compound packing voids, whilst in some areas planar voids give a zig-zag crack pattern. This development in microstructure may be due to an increase in wet

and dry cycles, producing the zig-zag cracks, and plant activity since many voids are associated with root sections. Textural pedofeatures occur in similar quantities to the BC_g but typic coatings and hypocoatings are more abundant suggesting a higher concentration of iron here, and its presence on void surfaces may serve to stabilise the structure that has developed. It is likely that this structure is reasonably stable since many voids contain more than one root structure, often in various stages of decay, suggesting that these voids have been in existence over a period of time. Occasional quasi-coatings occur which are rarely associated with organic residues. These may initially have been typic hypocoatings which have subsequently lost that iron deposited closest to the void surface through reduction during later anaerobic periods, the iron either being removed in the drainage waters or migrating into the matrix to regions of higher Eh. The absence of organic matter may have prevented the total reduction of these features.

The microstructure of the B horizon of the podzols is more complex. In the brown podzolic soil there is very little distinction between the upper and lower B_s (B_{s1} and B_{s2} respectively), both having subangular to angular blocks and ultrafine spheroidal crumb peds. Often, the blocks are porous and are possibly formed by coalescence of spheroidal crumbs. This structural type is also present in the B_{s2} of the stagnopodzol (fig 6.15g and h). The origin of such a fabric, described as "spongy" or "loose", is not certain. It is suggested by some authors (Maltby and Caseldine, 1982; Björkhan and Jongerius, 1988) that it has a biological origin, and certainly such crumbs do resemble soil faunal excrements, particularly those of earthworms. However, no other features associated with faunal activity in soils were evident, such as porostriated b-fabrics, although such features were occasionally noted in upland buried soils on Bodmin Moor by Maltby and Caseldine (1982); these may well have been better preserved due to the burial of the soil under Bronze age mounds.

Much of the literature on soil mesofauna is concerned with earthworms (*Lumbricidae*) or with faunal activity in the top 10-20cm of a soil, usually relating to the surface humus layers (Kuhnelt, 1961; Burgess, 1963; Wallwork, 1976). Species common in mor or peaty surface layers are reported to be *Acarina* (mites), *Collembola* (spring tails), *Diptera* and *Enchytraeidae*, and Wallwork (1976) suggested that, although such species may find their way into the mineral soil from time to time, they can never be regarded as more than transient in this environment. These species are generally classed as non-burrowers and non-ingesters of mineral particles, and therefore could not produce the structural units described. Burgess (1963) suggested that some protozoa require the components of mineral particles for

the production of shells, but this would involve the dissolution of mineral grains and so again not lead to the production of units with mineral inclusions.

Thus it is clear that under present-day conditions there are no biological agents in the soil that could produce such a structure, and the presence of an ironpan would also tend to exclude most mesofauna and roots, so further reducing the level of biological activity. In present-day brown earth soils, earthworm activity has been reported at depths greater than 50cm, and therefore past earthworm activity could have produced these structural units, which have since undergone coalescence as a result of aging. However, several points seem to suggest that this may not be the origin of this characteristic fabric. Units are found at the deepest points sampled, and occur within cracks in stones, which can be <100µm in width, which, unless material had been transported into the cracks, would preclude earthworm activity.

An alternative is that such fabric is due to microbial activity, both during and after podzolisation. Researchers in the School of Biological Sciences at UWB have isolated a variety of iron reducing and oxidising bacteria from these soils (D.B. Johnson, pers. comm., 1994), who have suggested that bacteria, in secreting gums, can form and stabilise a fine crumb structure. This would explain the persistence of many of the cutans in an undisturbed state which earthworm activity would not. This is very similar to the idea proposed by Aristovskya (1958; 1963) and also implies current activity in the podzol.

However, there are again problems with this solution. Earthworm and microbial activity in soil lead to the presence of polysaccharide gums, which can bind soil particles together and provide structural stability for peds. However, these only last in a soil environment for $n \times 10$ years (D. B. Johnson, pers. comm., 1994) and therefore could not explain the preservation of these structural units for $n \times 1000$ years.

It is obvious that the main cementing agent now is oxidised iron. A test for polysaccharide presence and quantity may help evaluate the role of microbes at the present-day, but with values of organic carbon in the BC below 1% this is unlikely to be significant. Thus, it would appear that past or present biological activity cannot provide a satisfactory solution to the problem of structural development of the B_s spongy fabric. It is likely, therefore, that this structure has developed primarily by physical processes - wetting/drying cycles and stabilisation of peds by iron. This would account for the depth of such peds in the profiles and their presence within cracks in stones. It is also possible that colloidal allophanic glues have a role to play

since it is assumed, from chemical data, that such material is present in these soils even though none could be detected by micromorphological techniques.

The micromorphology of the upper B_s of the stagnopodzol differs from this in that peds are subangular blocks and the porosity is lower. There is also an increase in the quantity of nodules (fig 6.15i and j) and this suggests that this part of the B_s is influenced by hydromorphic processes, leading to a mobilisation and concentration of iron into nodules and a general paling of the soil colour. This may be a movement of iron from above, but the paling of the upper B_s in some areas suggests a redistribution of iron within the B_s horizon itself. It is possible that this is an effect of the increasing thickness of surface peat since this differentiation of the B_s is not noted in the brown podzolic soil which lacks a peaty surface horizon. The absence of a "spongy" fabric may represent a collapse of such peds as iron is mobilised and redistributed, since paler areas have a more massive microstructure, similar to that seen in gleyed horizons.

Lying between the B_{s1} and E_{ag} in the stagnopodzol is a "cemented" horizon (B_f), and this differs quite considerably in morphology and composition to the rest of the B horizon (Fig 6.15o). Porosity is low (5-10%) and the subangular to angular blocky peds are surrounded by planar voids with occasional vughs. Siltstone fragments occasionally exhibit pellicular alteration, and the fine inorganic fraction is stained red-brown suggestive of a high concentration of iron. The indurated nature of this horizon is indicated by the fact that most roots are restricted to the upper surface and are often deformed as a result of this restriction.

The fine organic fraction is presumed to be that found throughout the horizon, mainly as orange-red, isotropic dense complete void infillings or typical void coatings, frequently cracked (fig 6.15k and l). This is very similar to the materials described by other workers, such as De Coninck (1980) and Sanborn and Lavkulich (1989b). They described such features as "organans" or "monomorphic coatings", and have suggested that they are areas of metal accumulation (Al, K, Ca, Fe and Zn). De Coninck (1980) suggested that the strikingly cracked nature of these features indicated that there had been a transition from a gel to a solid and that this was consistent with organo-mineral compounds immobilised in a gel-state. However, there is the possibility that these cracks are the result of the drying of samples prior to impregnation, and that acetone replacement prior to the addition of resin may result in the absence of such cracks.

EDXRA results (Appendix Vh,i,j k and l) from Hiraethog samples confirm the iron-rich nature of such deposits, which usually also show higher sulphur content than the resin, suggesting the organic nature of the material. They do show, to some extent, the accumulations of Al, K, and Ca relative to Si as suggested by Sanborn and Lavkulich (1989b) but not the Al levels required for the proto-imogolite material noted by Farmer *et al.* (1985) from cemented horizons. There is also no marked accumulation of manganese in these deposits, an element often associated with Fe in such horizons. Mn accumulations are noted in the gley soils of Hiraethog, and their absence here may reflect a different Eh/pH regime. Bower (1970) proposed that the quantity of Mn in the Hiraethog series fine sand fraction could be attributed to the high content of manganese (1800ppm) found in chlorite and that there was a pronounced rise in Mn as a trace element in the Bf horizon, although this was for bulk samples and no data on the distribution of Mn within the pan was available.

6.4.2.3 A horizons

The surface mineral horizon of the stagnopodzol and stagnogley are similar micromorphologically. Both are dominated by subangular to angular blocky peds and spheroidal granules or crumbs, usually the latter having a clustered basic distribution within voids. These are probably excrement pedofeatures, mostly fresh although some coalescence into larger units does occur which may be a sign of their aging. The porosity of the Eag horizons is greatest where the material is stained brown, probably by organic pigmentation. This is possibly the result of greater soil faunal activity in these areas since these are also the areas of presumed excrement pedofeature accumulation. Stone-rim bleaching is a feature of this horizon, and Macphail *et al.* (1987) suggested that this is the result of the superimposition of gleying on a previously oxidised soil. However, such features are also noted throughout the B_s horizon which would indicate that this was not the case, at least in the lower, aerobic horizons. It has been postulated (Dr D.A. Jenkins, pers. comm.) that the presence of this feature in the B_s horizon may reflect the podzolisation processes, whereby there is a mobilisation of iron in the outer layer of a stone and its subsequent reprecipitation deeper in the fragment. This would explain the existence of stone-rim bleaching in an aerobic environment, which the previous theory (Macphail *et al.*, 1987) would not.

The surface horizon in the podzolised brown earth (A_h) has a microstructure very similar to the lower B_s, *i.e.* dominated by angular blocks and spheroidal granules. This surface structural type is interpreted as excrement pedofeatures which include mineral material suggesting that a thorough mixing of this horizon has taken place. These also

show signs of coalescence into porous peds which is thought to be a result of their aging. The whole of this horizon is stained brown, probably by organic pigmentation, and porosity is high, suggesting continual mixing by faunal activity, such as oribatid mites (circular excrements) and Julidae or Glomeridae (conoid excrements).

An important macro-feature of the brown podzolic soil is the ovoid feature noted in the B_s horizon, with a micromorphology very similar to that of the surface A_h horizon. This feature is interpreted as an infilled mole channel, the infill having originated in the surface horizon. This raises very interesting questions concerning the present-day soil fauna, which will obviously have implications for the soil micromorphology. If moles are present then one must presume that earthworms will also be present, since it has been shown that >90% of a moles diet is composed of earthworms (Godfrey and Crowcroft, 1960). However, pH values from these soils are <5, and from this one would not expect earthworms to survive. It is possible that the moles present 10m away from the sampled exposure of brown podzolic soil are existing in a pocket of brown earth type soil which contains earthworms, and that this feature noted in the B_s of the brown podzolic soil represents part of a nesting burrow, or the movement of moles between two sites with higher pH soils, one having been lost due to erosion of the ground surface by the fluctuating water levels in the reservoir. It is also likely that the distribution of earthworms and moles was greater in the past and has since contracted with the loss of suitable habitats due to soil acidification.

6.4.2.4 O horizons

The peaty surface horizons of the stagnopodzol and stagnogley are very similar. Both have peds composed of spheroidal crumbs and granules which grade into porous subangular blocky peds. It is likely that these horizons are substantially affected by faunal and microbial activity since this material shows little birefringence or UV auto-fluorescence, suggesting it is well humified. However, these peds do not have the inclusions of inorganic materials and are completely opaque, and so cannot be equated with similar peds found in B_s horizons. The lack of inorganic inclusions may simply reflect a lack of incorporation of such particles in this horizon rather than a different mode of formation.

6.4.3 Conclusions

Soil micromorphology can highlight many interesting features which aid the interpretation of pedogenic processes and the sequences in which they have occurred *i.e.* the microstratigraphic approach proposed by Kemp (1985a). This analysis has allowed the development of the different profile characteristics of the soils of Hiraethog to be more fully understood.

The staghomic gley soil, found in relatively flat, water receiving sites, was in the past better drained with aerobic conditions resulting in the existence of a darker coloured soil. Subsequent waterlogging and permanently gleyed conditions has meant that iron has been lost from the profile, structural units have collapsed and a massive soil has been the end result. Stone fragments have become totally rehydrated and are barely distinguishable from the rest of the soil fabric. It may be that the peaty surface accumulation caused, or at least enhanced, the waterlogging by increasing water retention at the surface of the mineral soil.

Interpretations can also be made concerning the development of the different podzolic profiles found around Aled Isaf. It is proposed (Avery, 1990) that these soils were both brown earth soils at some stage in their past. Certainly, both parent materials had undergone periglacial reworking resulting in a reorientation and cracks in stone fragments. Both the brown podzolic soil and the ironpan stagnopodzolic soil were influenced by limited clay translocation, often in phases interspersed with periods of soil disturbance resulting in the movement and deposition of coarser-grained material due to vegetation disturbance or periglacial activity. In both podzolisation processes have taken place to produce the characteristic B_s podzol horizon. However, it is at this stage that the brown podzolic soil remains today. The ironpan stagnopodzol profiles have thin, pale argillans, not noted in the brown podzolic soil, and these may relate to a greater intensity of weathering in the former. However, no amorphous allophanic material could be identified by these micromorphological techniques.

It is likely that podzolisation processes followed clay translocation, and these were followed by the formation of the characteristic spongy B_s fabric. The ironpan stagnopodzol also has an ironpan, an E_{ag} horizon and a surface peaty layer. The ironpan is a zone of iron concentration, has a very compact structure and is a barrier to some root penetration resulting in an overlying layer of organic matter. There is slight Al, but no distinct manganese, accumulation. The E_{ag} has a massive structure,

similar to that of the gleyed soil, and it is likely that this has resulted from a loss of iron compounds through gleying and a collapse of structural units. The presence of stone rim bleaching suggests that this horizon was at one time not gleyed and of a darker colour.

There is a differentiation possible between the upper and lower portions of the B_g horizon of the ironpan stagnopodzol, one which is not noted in the brown podzolic soil. This is in the form of a paler colour and a more massive structure for the B_{g1}, along with a higher concentration of nodules. This seems to indicate a redistribution of iron, either into nodules or out of the horizon, causing a breakdown of structural units and a paling of the horizons colour. This is suggestive of progressive gleying processes, and may indicate an increasing influence of the surface peaty horizon as it gets thicker.

Therefore, from micromorphological evidence alone, some information can be gained concerning the pedogenic processes that have operated in the soils in the past and at the present day, and the sequence in which they have occurred.

6.5 The timing of the formation of the ironpan stagnopodzol soil profiles studied around the margins of Aled Isaf.

Figure 6.16 (Dr D.A. Jenkins, in Avery 1990), presents the results of the only study previously carried out at this site with the intention of dating the formation of the striking profile characteristics of the ironpan stagnopodzol. Of particular interest to this study is the suggested rapid build up of the soil profile during the period 6,000 to 4,000 years BP and the timing of formation of the ironpan in relation to the accumulation of peat at the surface of the mineral soil.

The radiocarbon dates presented in Avery (1990) were carried out by Scharpenseel in the 1970's, but no details of preparation techniques or error assessment are available at the present time. Dating of peat and charcoal samples is fairly straightforward, as long as all the problems outlined in section 4.8 are taken into account. However, as detailed in section 4.8.4, there are more difficulties associated with the dating of organic matter incorporated into the mineral soil, such as the ironpan, and this part of the research programme set out to limit these as far as possible to obtain the most accurate date for the initial formation of the ironpan in these soils.

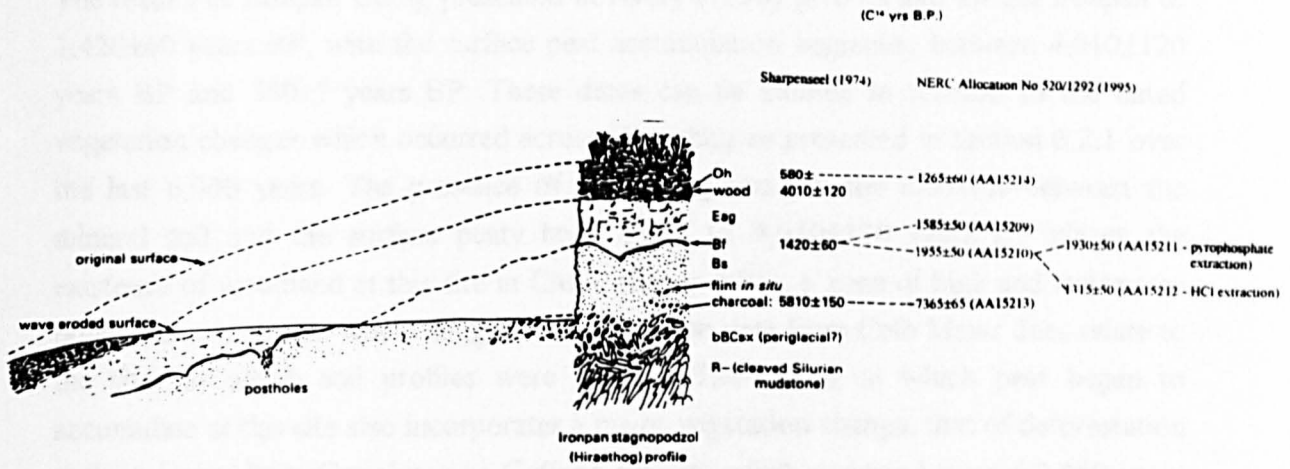


Figure 6.16 Exposure of a stagnopodzol profile at Aled Isaf (from a drawing by Dr D.A. Jenkins in Avery, 1990 incorporating dates obtained during this research project).

The data presented in figure 5.2 outlines the composition of the ironpan in terms of its extractable organic carbon, aluminium and iron. These analyses were carried out on fragments of ironpan from which all underlying and overlying horizon material had been physically removed, including the layer of roots in various stages of decay which builds up on the surface of the pan. Therefore, the quantities of extractable carbon relate to that material actually held within the pan, possibly in the form (red-brown, isotropic, cracked) as described in the micromorphological investigations (section 6.4).

One of the main problems in studying the time of formation of an ironpan is that it is unlikely that it was produced in one phase, and it may be that formation, and so carbon incorporation, occurred over a more protracted time span, such that dating of a bulk sample would give a date younger than the initial time of formation, *ie.* the mean residence time (MRT). It was for this reason that a study was undertaken, with financial and technical support from NERC Scientific Services, of the different fractions of organic C in the ironpan. The results (figure 5.2) showed that the ironpan contained around 6% total organic C, of which up to 5% was extractable by pyrophosphate and 4% by Na-dithionite. HCl left a similar quantity of organic C in the residue to pyrophosphate. Since it was necessary to remove as much "young" organic C as possible, dating by the AMS technique was undertaken on the residues left after extraction by 0.1M pyrophosphate and by 6M HCl, as well as of a bulk sample for comparison purposes (as described in Appendix VIb).

The results of ironpan dating presented in Avery (1990) give an age for the ironpan of $1,420 \pm 60$ years BP, with the surface peat accumulation beginning between $4,010 \pm 120$ years BP and $580 \pm ?$ years BP. These dates can be studied in relation to the dated vegetation changes which occurred across Hiraethog as presented in section 6.2.1 over the last 6,000 years. The presence of wood fragments at the interface between the mineral soil and the surface peaty layer dated to $4,010 \pm 120$ years BP places the existence of woodland at this site in CM1c (figure 6.21), a zone of high and stable tree pollen values and this would suggest that the pollen data from Cefn Mawr does relate to the sites at which soil profiles were studied. The period in which peat began to accumulate at this site also incorporates a major vegetation change, that of deforestation with a change from Gramineae to *Calluna* species, which occurred around 2,060 years BP. Pollen evidence from the surface peat suggests that peat accumulation did in fact begin at this point.

The fact that the date given for the ironpan is older than that for the base of the peaty surface horizon suggests that the theory first proposed by Muir (1938), that peat accumulation caused the formation of E_{ag}/B_f horizons, is not correct, the opposite to that indicated by other evidence used to support this theory earlier in this thesis (clay mineralogy and micromorphology). It is, however, possible, with all the problems associated with the dating of soil materials, that the date presented in Avery (1990) for the B_f horizon may be even older, although no further comment can be made on this point without knowledge of the preparation techniques used by Professor Scharpenseel.

These dates and their interpretation can now be studied in relation to the AMS ^{14}C dating carried out for this research project. The base of the O_h horizon was dated to $1,265 \pm 60$ year BP, a date over twice as old as that presented in Avery (1990). This latter, $580 \pm ?$ years BP, would have required at least 2g of organic carbon since AMS dating was not available then, and this may have increased any inaccuracies. However, it is possible that both dates for the base of the peaty surface horizon are in error due to contamination by younger carbon, since this horizon is rarely more than 20cm in depth, and chemical analyses of the underlying mineral soil indicates that there is movement of organic carbon down the profile. These dates must therefore be only minimum ages for the onset of peat accumulation. It is therefore difficult to be conclusive about the timing of the onset of peat accumulation at this site. On the other hand, the difference between the two dates may be real simply reflecting slightly differing site conditions, although again there is no record of the location of the profile sampled by K. Stahr for Scharpenseel.

The dates for the ironpan obtained for this research are also of interest. Two samples of untreated ironpan were dated from different profiles, which gave dates of $1,585 \pm 50$ and $1,955 \pm 50$ years BP, differing by nearly 400 years. This could again be a result of slightly differing site conditions for the two profiles and not due to errors often associated with the preparation and dating procedures. The fact that one date for the ironpan from profile 1 is very close to that presented in Avery (1990) suggests that either there are not substantial errors or the errors are consistent in both sets of dates presented.

However, as outlined earlier, an attempt was made to fractionate the organic carbon held in the ironpan to reduce contamination by younger carbon. Both techniques used, 0.1M pyrophosphate and 6M HCl, left similar amounts of organic carbon in the residue after extraction ($\approx 1.5\%$), and 6M HCl is widely regarded as being a valuable pretreatment to remove young hydrolysable carbon from samples. Na-dithionite was not used in this study because of the need to use an organic (citrate) buffer to maintain the pH during the extraction.

The results of this study, carried out on only one sample of ironpan, highlight the lack of understanding concerning the development of ironpans and the role of organic carbon in this process. The two bulk samples dated differed by about 400 years, which as suggested may reflect differing site conditions at the present-day and in the past. Extraction of sample 2 by pyrophosphate resulted in no real change in the age of the residual organic carbon in the pan. This lack of change in age after treatment with pyrophosphate are consistent with the high Fe_d/Fe_p ratios detected in this horizon (Table 6.2) which indicated that the horizon was relatively stable, and that additions of iron, and therefore possibly carbon, were only occurring at the surface of the pan. Thus the age obtained for the bulk sample may represent the age of the oldest carbon fraction.

The treatment with 6M HCl resulted in a reduction in age by some 600 years. This is contrary to that expected and the reason for this is not totally clear, especially since the test was carried out on only one sample and so no comparative data are available. However, it is known (R. Bol, pers comm, 1995) that hydrolysis of leaf litter will result in a younger age for a sample if there are large quantities of hydrolysable sugars, and it may be that this is the case here, or that iron is stabilising organic carbon in a form that can be easily hydrolysed. A better understanding of the form that carbon is in within the pan may help resolve some of these problems. However, as mentioned earlier, this study looked in detail at only one sample of ironpan, and a better understanding of the situation would require more extensive analysis and dating of the different fractions of organic carbon in the ironpan.

The results presented in Avery (1990) raise another very interesting point concerning the development of these ironpan stagnopodzol profiles. The dating suggests that up to 50cm of profile accumulated in the period 5,810±150 years BP to 4,010±120 years BP, a period of under 2,000 years. It is very unlikely that weathering could have produced such a depth of soil in this time, and therefore it is possible that soil erosion and redeposition downslope was the cause. This would also explain the burial of charcoal fragments at this point in the profile. This time period coincides with the phase when, from archaeological evidence, Mesolithic man is thought to have been present at the site, and the local pollen assemblage zones CM1a and b when it is likely that fires, caused by human activity, resulted in periodic openings in the forest canopy with subsequent exposure of the soil surface to more intense erosive forces, particularly rain-drop impact and surface runoff. There is no micromorphological evidence of colluviation at these sites although no systematic analysis of stone orientation in thin section has been undertaken.

The evidence in the literature on present-day soil erosion events (Boardman *et al.*, 1990; Arden-Clarke and Evans, 1993) all points to the fact that soil erosion is greatest where the surface vegetation and/or the soil surface has been disturbed, usually by factors instigated by human activity, such as deforestation, overgrazing, ploughing and moorland burning. However, much less is known about the timing and causes of past erosion events. That they occurred has become evident from the study of sedimentary sequences by archaeologists and palaeobotanists (*e.g.* Vuorela, 1983). It is suggested (Evans, 1990) that the attempts by Mesolithic man to clear woods by axe and fire, although usually on a small scale, may still have resulted in localised erosion events. From a review of the literature, Evans (1990) also suggested that by the Bronze Age the conversion of land for arable farming may have led to an intensification of erosion.

The dates presented here indicate a phase of erosion at this site, and it is possible that this was occasioned by the activities of man. However, the dates relate to a single soil profile; if a similar event can be recognised over a wider area then it may be necessary to look for some other explanation for a more extensive erosion event. Additional data on this problem are supplied by the dating of charcoal fragments (*Alnus*) from the base of the profile, the presence of charcoal often being used as a criterion for the identification of colluvial material (Courty *et al.*, 1989). Avery (1990) quotes a date of 5,810±150 years BP for charcoal in a similar position, whilst the date obtained for this research is 7,365±65 years BP (8,124 years cal BP). However, for this profile no wood fragments were noted from the top of the mineral soil, and so no comments can be made concerning the rate of profile build up at this site. It does, however, suggest that the land

surface at this site was considerably lower in the Mesolithic, and that some process has occurred to result in the burial of such charcoal fragments which can be up to 1 cm³. This is likely since all the profiles studied lie in the lower slope facets and would be expected to be receiving sites for eroded material. It is likely that such fragments were buried soon after their deposition on the soil surface since exposure to the elements would have led to their disintegration, unless they are parts of root which were burned *in situ* beneath the surface of the soil profile. The lack of pith in any of the samples recovered makes it impossible to determine from which plant parts the charcoal came (Dr P. Denne, pers. comm., 1995)

However, if these dates do indicate the true sequence of events that have occurred at this specific site, some of the interpretations made earlier, especially concerning the existence of some of the features noted during the micromorphological investigation, need to be revised. The above data indicate that up to 6,000 years ago the soils present were shallower and would also have been of a much coarser texture. Interpretations of micromorphological features previously suggested that the presence of argillans and the banding of these with coarser material was related to the periodic disturbances that occurred in the vegetation community during local pollen assemblage zone CM1b. This may still be a valid argument in that the deposition of material at the surface of the profile may have provided an abundance of fine grained materials to be washed down the profile and subsequently deposited. However, it may be that these argillans, including the coarse-grained materials, were formed prior to the erosion event when the soil was shallower and of a coarser texture, possibly relating to disturbance during periglacial conditions which are known to have operated on Hiraethog and would have involved a sparse vegetation cover (see section 6.2), an interpretation suggested by Dr D.A. Jenkins (pers. comm., 1995). Their subsequent burial and isolation from disturbance may be the reason that they are still to be noted in the profiles at the present-day, but only in the lowest horizon, the BC. Their presence in only the BC horizon, in material older than at least 6,000 years also indicates that the vegetation fluctuations noted in CM1 were not responsible for their formation since no such cutans are present in the overlying horizons, and that significant clay and silt translocation had ceased by this time, even though the vegetation community indicate the existence of fertile, high pH soils. All this lends weight to the proposal that these are periglacial features, formed under fluctuating freeze/thaw seasonal climatic conditions.

These dates also indicate that since the pale or red-brown argillans are found in the Bs horizons of the podzols, above the layer of charcoal concentration, then these features must relate to processes that have occurred since around 6,000 years BP.

6.6 Tephrochronology.

6.6.1 Results

This study had been undertaken in an attempt to locate tephra layers, initially by the X-raying of core sections since tephra is more X-ray dense than peat. However, only one section revealed a feature similar to those described by Dugmore (1989) for peats in Scotland. Radiocarbon dates suggested that this point in the Llyn Cororion core related to the Hekla 3 eruption on Iceland in 1120 ± 50 BC (Hammer *et al.*, 1980). Four potential tephra locations were analysed from the Llyn Cororion core, whilst no X-ray dense material was highlighted in the Cefn Mawr core. The results for the extractions carried out on samples from the Llyn Cororion core are presented in tables 6.7 and 6.8.

Table 6.7 Ashing/weak acid digestion of samples from Llyn Cororion core.

Sample	1	2	3	4
Age estimate (^{14}C yrs BP)	3122	3366	4690	4722
Depth from top of core (cm)	246.5-247.0	264.5-265.0	370.0-370.5	372.5-373.0
Weight of sediment (g)	3.75	3.14	5.19	4.28
Weight of residue (g)	0.09	0.12	0.05	0.04
% inorganic material	2.40	3.82	0.96	0.93

From the X-radiographs one possible layer of fine-grained inorganic material was located at 246.5-247.0cm (1) from the top of the Llyn Cororion core (Lascelles, 1993). At 264.5-265.0cm (2) there was an inclusion of coarser grained material, whilst at the last two points (3 and 4) little inorganic material was highlighted. Sample two, which did not contain detectable tephra, probably relates to an erosion event on the land surrounding Llyn Cororion, with short distance transport of material due to the grain sizes present (up to 2mm). The difference in percentage inorganic matter between sample 1 and samples 3 and 4 possibly accounts for the material being shown up as X-ray dense.

On analysis of the inorganic residue from sample 1 it was found that this material was not composed of tephra, but was dominated by diatoms and sponge spicules. The

species of diatom included *Pimularia*, *Eunotia pseudoveneris*, *E. subtaeniata*, *Gomphonema acuminatum* and *Melosira islandica*. The last two species are quoted as being alkaphilous (Haworth, 1976; Battarbee, 1978) whilst the two *Eunotia* species and *Pimularia* are usually categorised as acidophilous. However, all have been shown to dominate in the Post-Atlantic period which fits in with the date quoted (3,122 years BP) for this point in the sediment core.

Table 6.8 Biolith counts from sample 1. (Total count 583 bioliths).

Species	%	Comments ^a
<i>Gomphonema</i>	3.95	Indifferent ¹ ; Alkaphilous ^{2,4} ; Early Post-Atlantic ³
<i>Eunotia</i>	5.59	Acidophilous ^{3,1} ; Unknown ²
<i>Tabellaria</i>	1.48	Acidophilous ^{1,4} ; Unknown ² ; Post-Atlantic ³
<i>Cymbella</i>	3.45	Indifferent ^{2,4} ; Post-Atlantic ³
<i>Fragilaria</i>	0.99	Characteristic up to Mid-Atlantic ³
<i>Cyclotella</i>	2.20	Post-Atlantic ³ ; Indifferent ^{1,2}
<i>Pinnularia</i>	21.05	Acidophilous ² ; Unknown ¹ ; Indifferent ⁴
<i>Melosira</i>	6.08	Atlantic ³ ; Indifferent ¹ ; Alkaphilous ^{2,4}
Sponge spicules	27.80	Mainly whole ∴ not aeolian
Unidentifiable fragments	7.41	

a. Terms refer to preferred known habitat or Holocene period when species were most characteristic.

1. Evans and Walker (1977)
2. Battarbee (1978)
3. Round (1957)
4. Haworth (1976)

6.6.2 Discussion

The high concentration of opaline silica at this point raises an interesting question concerning the potential mobility of tephra-derived silica (Lascelles, 1993). Previous studies (Jewell, 1935) have shown that the formation of normal sponge spicules under freshwater conditions requires a silicic acid concentration of 0.005mM or greater, with only one instance reported where normal spicules were formed when only traces of silicic acid were present. A similar response has been noted in diatoms

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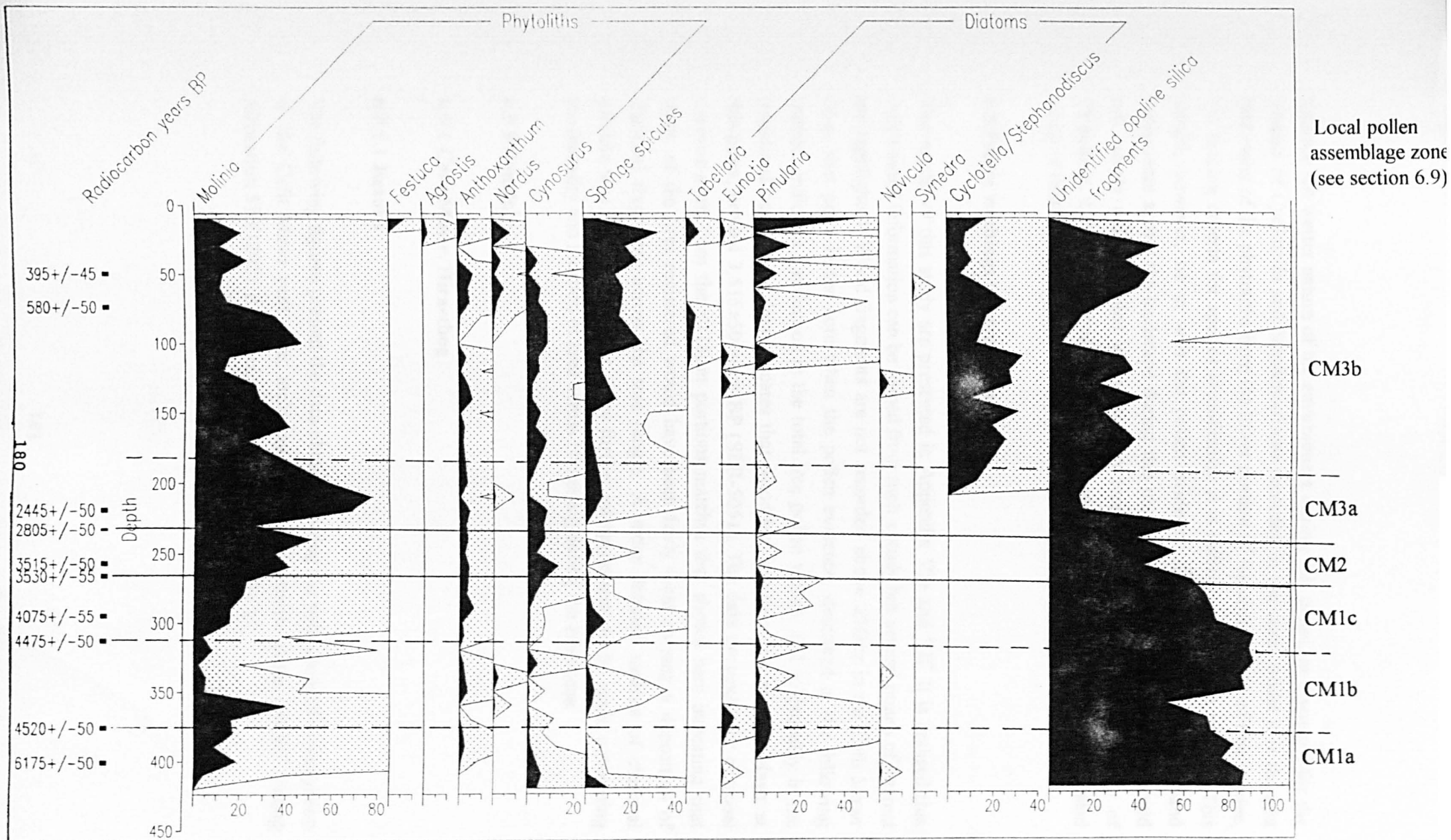


Figure 6.17 Bioliths recorded in samples of the Cefn Mawr peat core.

indicate the wetter nature of the environment during this phase, as discussed for the species of *Cyclotella* and *Stephanodiscus* recorded in the core, whilst it is thought that many of the phytoliths from the lower portion of the core may be of tree species, but lacking criteria for species identification it is difficult to be more specific. This would, however, tie in with the pollen evidence suggesting a larger woodland component across the landscape during this phase. Thus, although this study could not supply much detailed information in terms of the environmental history of Hiraethog, it does correspond to the pollen evidence presented, and a more detailed study of these fossils might well supply valuable additional data.

6.8 Pollen washings (macrofossils)

The results of this study are presented in Appendix VIe and VI f. It is realised that only limited information can be gained from such a study but several points of interest are highlighted. Wood fragments are not recorded above 250cm in the Cefn Mawr core, that point in the core when the pollen evidence, described in the following section, indicates a reduction in the total tree pollen values, and so probably in the woodland cover. This data indicates that woodland loss occurred at Cefn Mawr at this point, around $3,515 \pm 50$ years BP (SRR-5051). The data presented for charcoal concentration from the $<118\mu\text{m}$ portions matches that shown here indicating that many of the fires registered would have been fairly local causing a deposition of charcoal fragments across the size ranges. A more detailed analysis of charcoal particle size distribution might allow further interpretations to be made concerning the intensity and location of fires across Hiraethog during the Holocene.

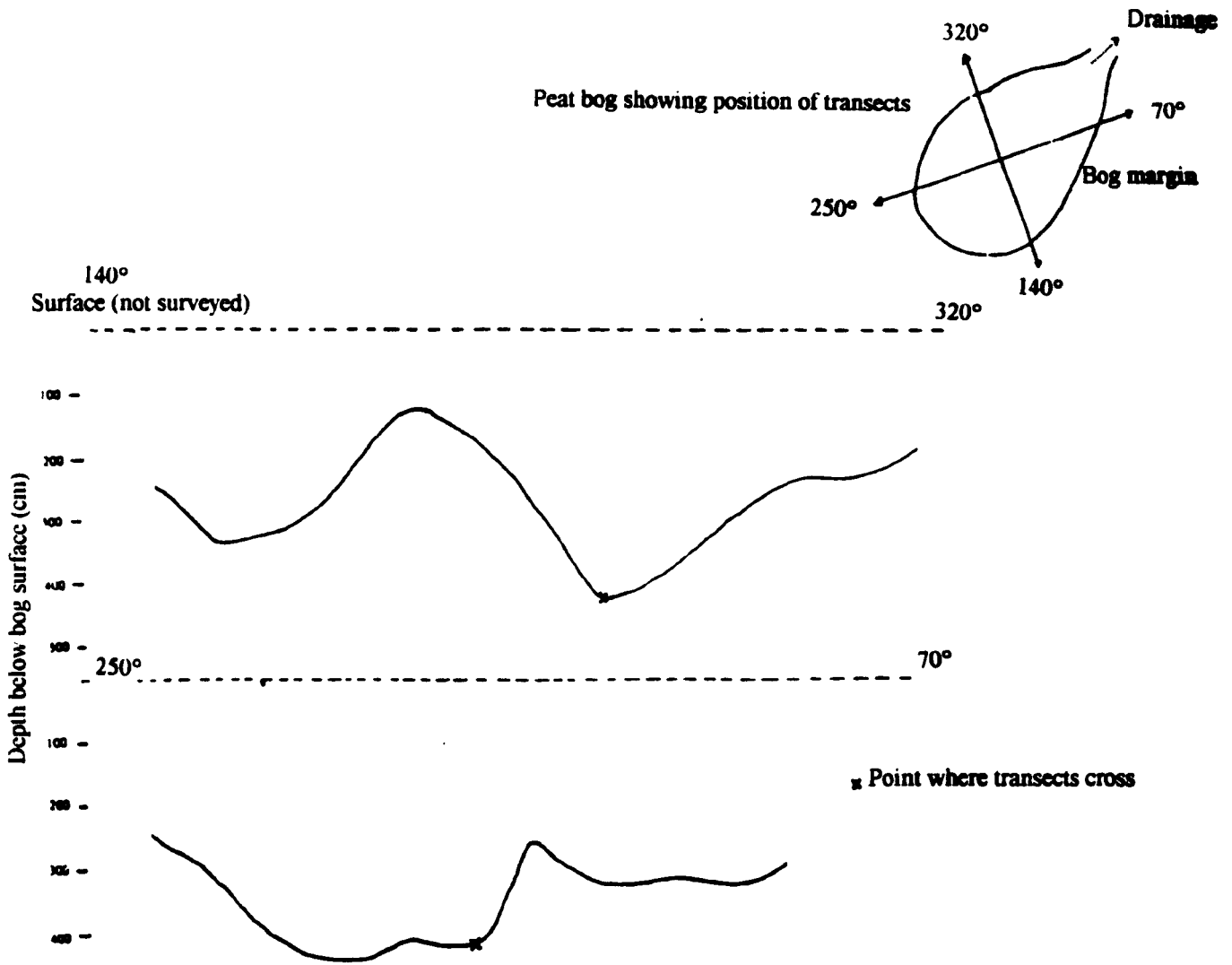
6.9 Palynology

6.9.1 Cefn Mawr, Hiraethog

6.9.1.1 Results

The following figures present the data obtained during the palynological investigation of the Cefn Mawr peat core, including the 10 radiometric dates (NERC Dating Allocation 510/1292). Raw data are presented in Appendix VI.

Figure 6.18 Depth of sediment below the surface of Cefn Mawr probed along two transects using steel rods.



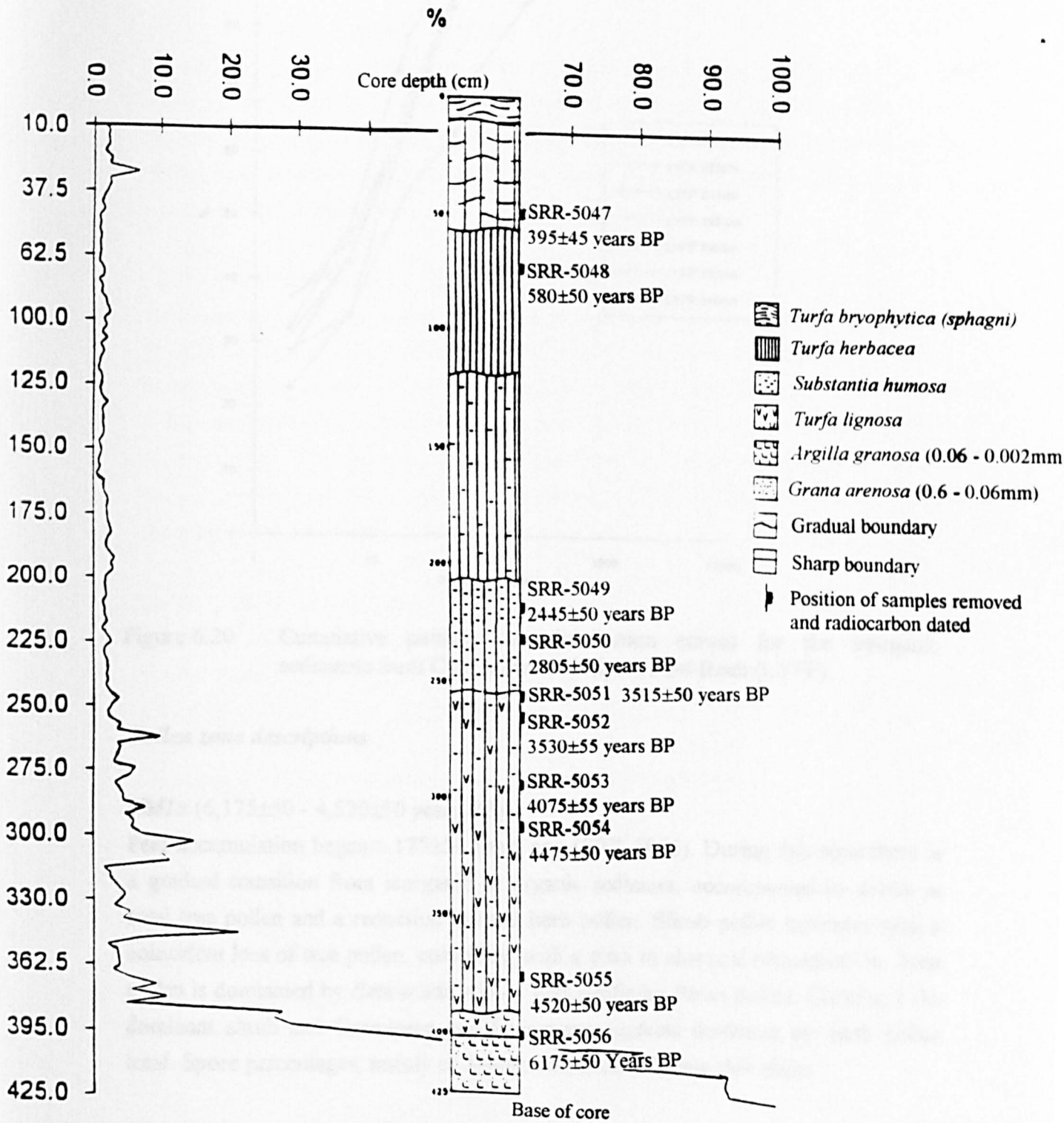


Figure 6.19 Core stratigraphy, ^{14}C dates and loss-on-ignition (ash content) data for the Cefn Mawr core.

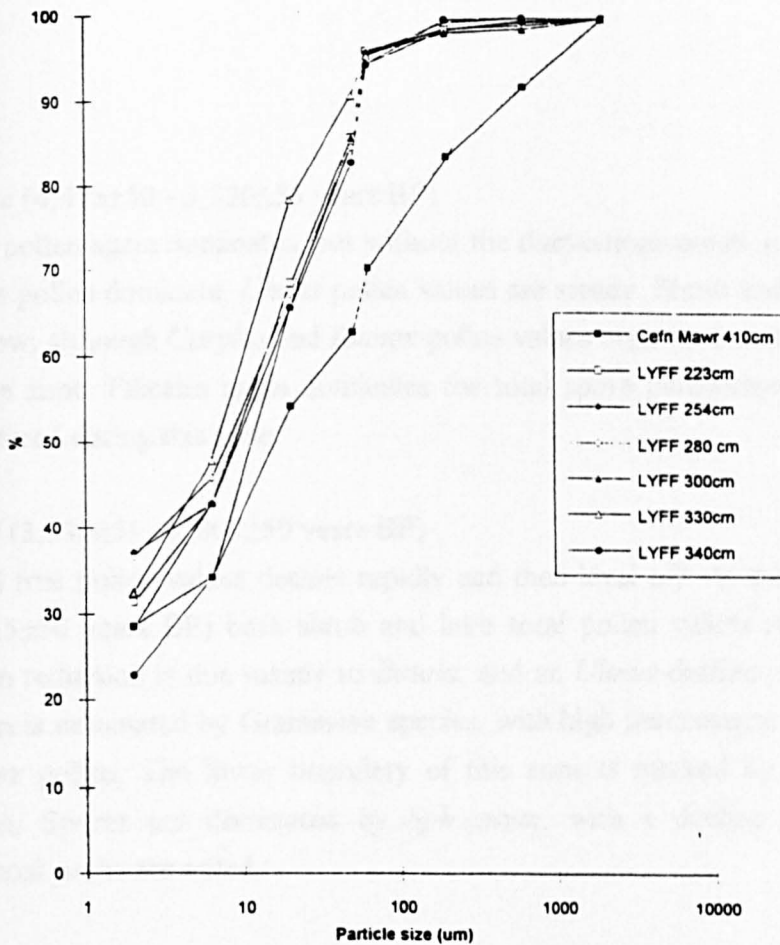


Figure 6.20 Cumulative particle size distribution curves for the inorganic sediments from Cefn Mawr and Llyn y Foel-frech (LYFF).

Pollen zone descriptions

CM1a (6,175±50 - 4,520±50 years BP)

Peat accumulation began 6,175±50 years ago (SRR-5056). During this zone there is a gradual transition from inorganic to organic sediment, accompanied by a rise in total tree pollen and a reduction in total herb pollen. Shrub pollen increases with a coincident loss of tree pollen, coinciding with a peak in charcoal concentration. Tree pollen is dominated by *Betula* and *Alnus*, with declining *Pinus* pollen. *Corylus* is the dominant shrub and Gramineae and Cyperaceae species dominate the herb pollen total. Spore percentages, mainly of *Sphagnum*, decline during this phase.

CM1b (4,520±50 - 4,475±50 years BP)

Tree pollen dominates, but fluctuates in response to shrub pollen increments. Two increases in total herb pollen occur. These changes coincide with peaks in the concentration of charcoal. Tree species dominating are *Betula* and *Alnus*, with some *Quercus*. *Pinus* pollen values continue to fall, and *Ulmus* pollen fluctuates. Increases in shrub pollen are due mainly to *Salix* pollen. Herb pollen is dominantly of Gramineae species, and Filicales dominates the total spore percentage.

CM1c (4,475±50 - 3,530±55 years BP)

Tree pollen again dominates, but without the fluctuations noted in CM1b. *Betula* and *Alnus* pollen dominate, *Ulmus* pollen values are steady. Shrub and herb pollen values are low, although *Corylus* and *Rumex* pollen values begin to increase towards the top of the zone. Filicales again dominates the total spore percentage. Little charcoal is registered during this zone.

CM2 (3,530±55 - 2,805±50 years BP)

Total tree pollen values decline rapidly and then level off. At this leveling off point (3,515±50 years BP) both shrub and herb total pollen values remain steady. Tree pollen reduction is due mainly to *Betula*, and an *Ulmus* decline is also noted. Herbs pollen is dominated by Gramineae species, with high percentages of *Filipendula* and *Rumex* pollen. The lower boundary of this zone is marked by a peak in *Nuphar* pollen. Spores are dominated by *Sphagnum*, with a decline in Filicales. Three charcoal peaks are noted.

CM3a (2,805±50 - 2,060 years BP)

Total tree pollen values continue to decline, but with fluctuations in increasing herb pollen totals, coinciding with peaks in charcoal concentration. *Ulmus* pollen continues to decline and Gramineae pollen dominates the total herb pollen values, together with *Filipendula* and *Rumex*. The first registration of *Plantago* pollen occurs during this phase. *Sphagnum* spore values remain high but fluctuate.

CM3b (2,060 - present-day)

Continued steady decline in total tree pollen with a replacement by herb pollen. *Calluna* pollen dominates over Gramineae pollen and *Plantago* pollen values increase. *Ulmus* pollen is lost from the sequence during this phase. Spore totals continue to be dominated by *Sphagnum* and further charcoal peaks are registered. *Pinus* pollen values increase again at the top of the core.

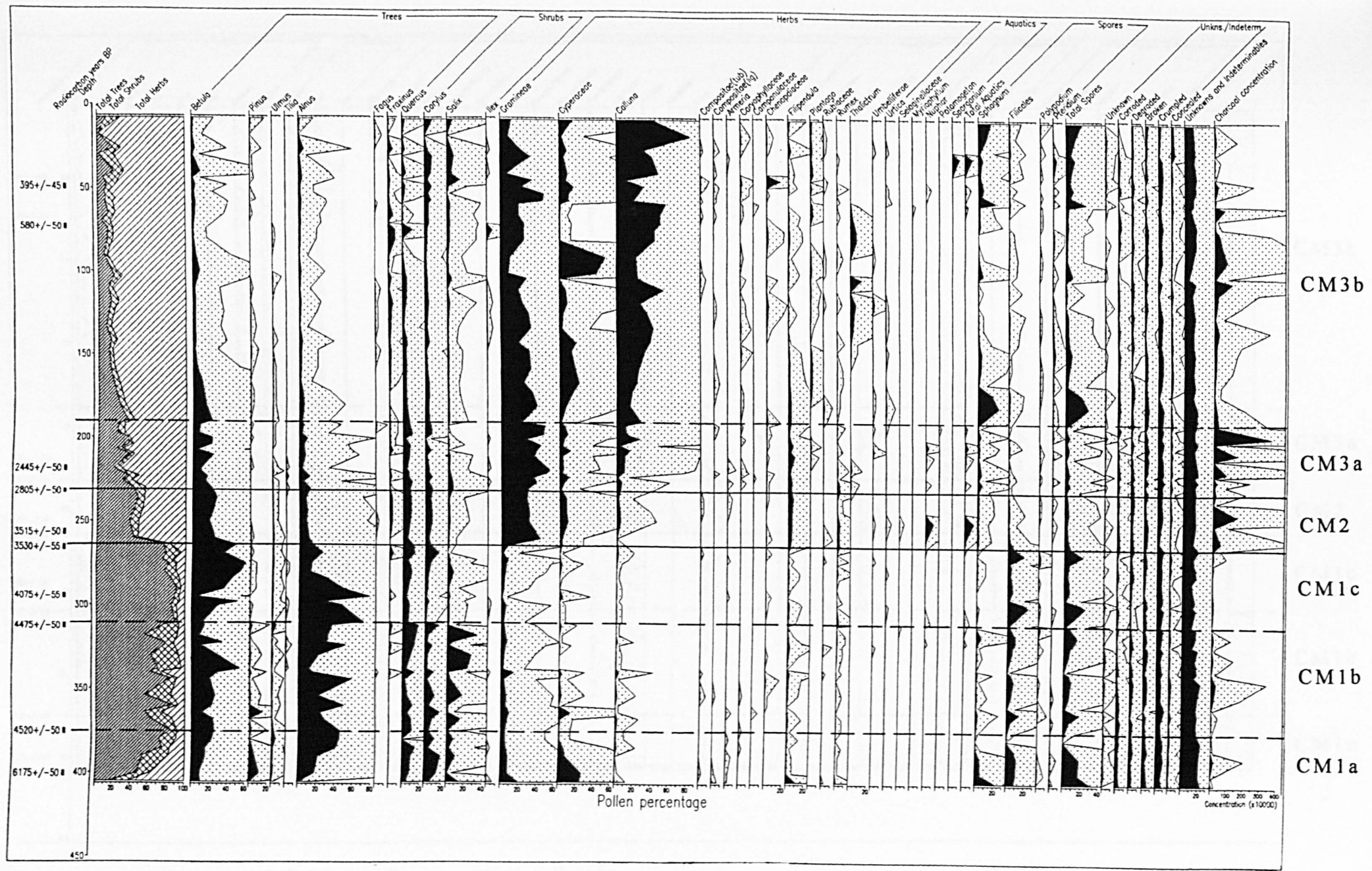


Figure 6.21 Cefn Mawr pollen percentage diagram.

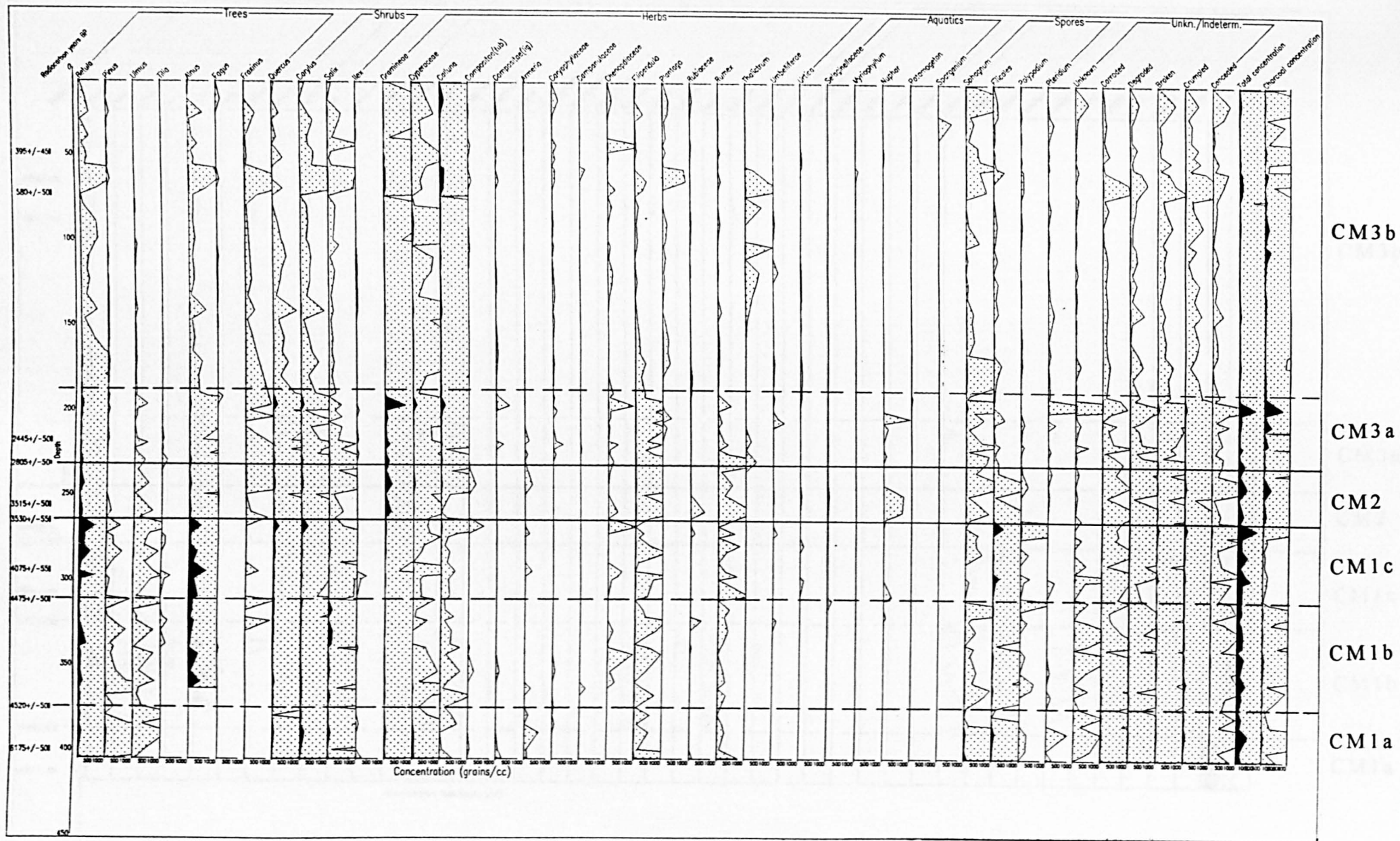


Figure 6.22 Cefn Mawr pollen concentration diagram.

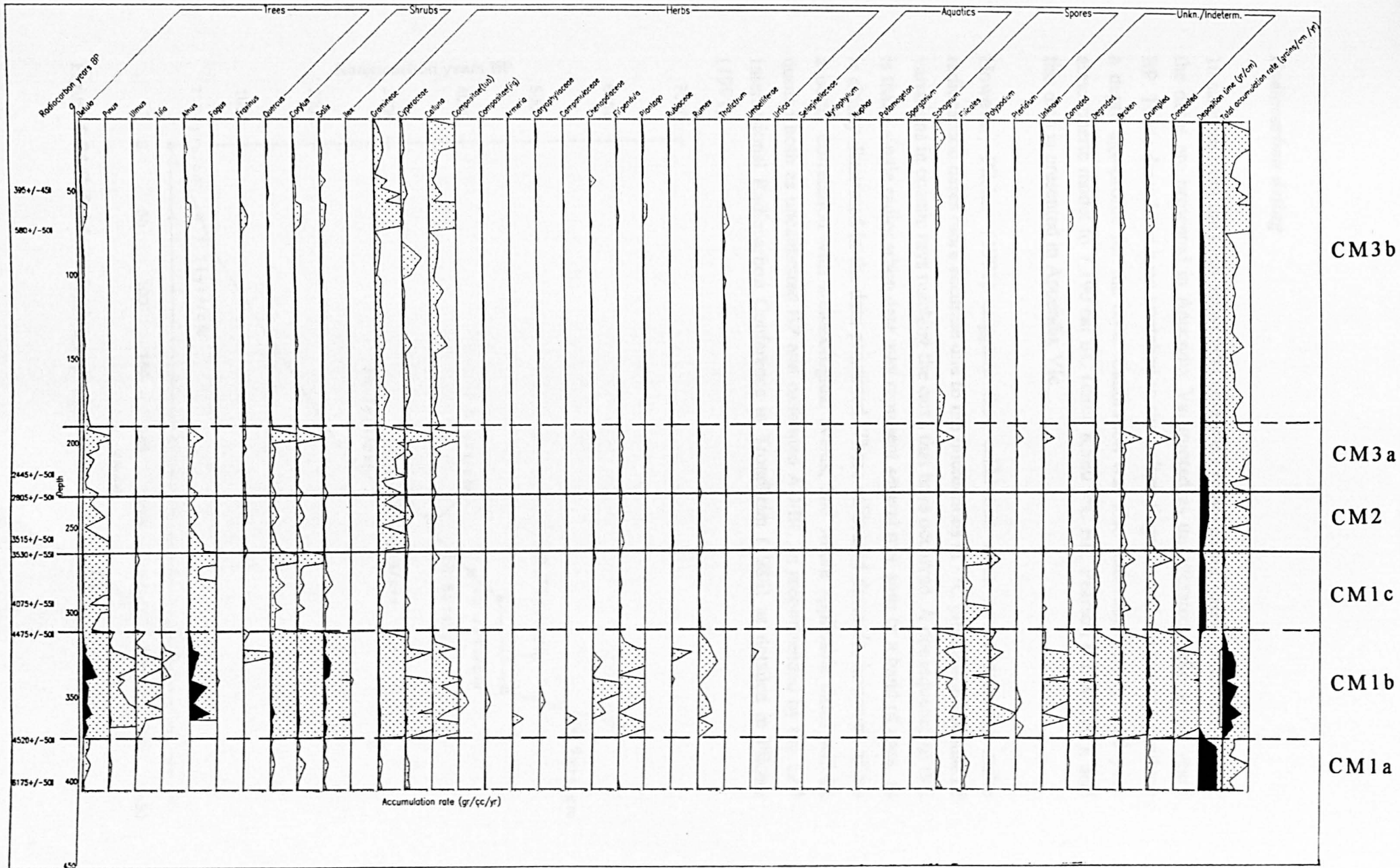


Figure 6.23 Cefn Mawr pollen accumulation diagram.

Radiocarbon dating

10 samples from the Cefn Mawr peat core were removed for dating (radiometric) and the dates are presented in Appendix Va, quoted as uncalibrated radiocarbon years BP. These dates have been attached to the pollen diagrams and are used to produce a depth age-profile for the core. Calibration was also undertaken using a 20 year atmospheric model to 7,190 cal BC (circa 8,580 ^{14}C BP; Pearson and Stuiver), and this data is presented in Appendix VIc.

However, Pilcher (1991) suggests that calibration does not necessarily make radiocarbon dates more accurate due to the fluctuations in ^{14}C production because of variations in cosmic rays reaching the earth that have occurred. A consequence of this is that a single radiocarbon date may represent several true ages or a band of ages, as is clearly illustrated in the data presented. These calibrated dates do, however, allow a better correlation with archaeological events, and where applicable dates will be quoted both as uncalibrated BP and calibrated AD/BC as recommended by the 12th International Radiocarbon Conference in Trondheim (1986) as detailed in Pilcher (1991).

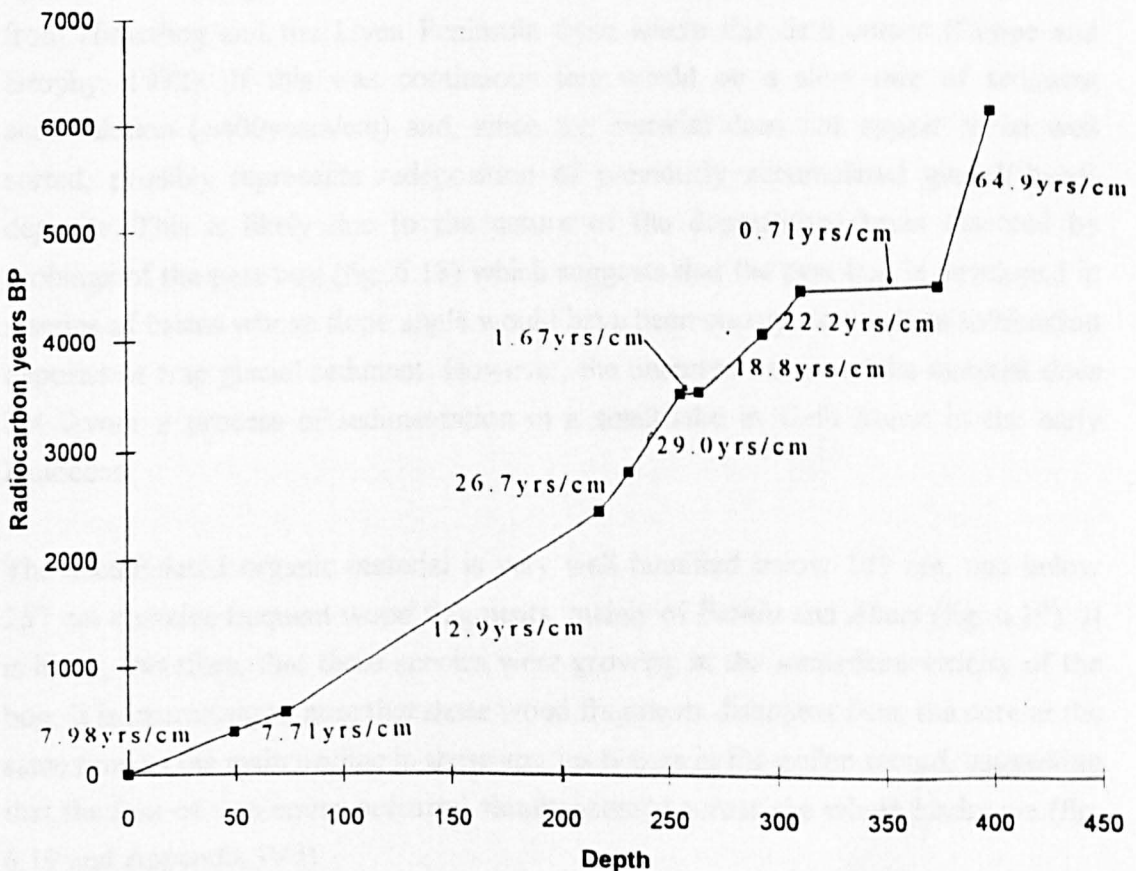


Figure 6.24 Cefn Mawr depth-age profile.

6.9.1.2 Discussion

The core retrieved from the peat bog on Hiraethog was 425cm in length. The bottom 20cm was composed of inorganic clay, silt and sand, with occasional siltstone fragments up to 5mm in size. Particle size analysis (fig 6.20) of this showed it not to have been well sorted, suggesting a glacial/periglacial origin. However, for particle size analysis a 50g sample was required, which meant removal of a 7cm core section. Whilst no stratification of this portion was visible, it may have been better sorted at a level <7cm than appears to be the case. This is a large sampling error, but one that cannot be avoided when core sections are narrow. An alternative to the hydrometer/sieving method may be to impregnate the core with resin and produce vertical thin sections as described in Chapter 5. In this way the grain-size distribution could be studied and quantified microscopically. Alternatively, the Sedigraph could be utilised since this only requires samples of around 10g which would enhance the resolution.

Organic matter accumulation began at $6,175 \pm 50$ BP (SRR-5056) and continued to the present day. This means that the 20cm of inorganic sediment below this accumulated during the period 14,000 to 6,000 BP, assuming synchronous ice loss from Hiraethog and the Llyn Peninsula from where this date comes (Coope and Brophy, 1972). If this was continuous this would be a slow rate of sediment accumulation (≈ 400 years/cm) and, since the material does not appear to be well sorted, possibly represents redeposition of previously accumulated glacial/"head" deposits. This is likely due to the nature of the depositional basin detected by probings of the peat bog (fig. 6.18) which suggests that the peat bog is developed in a series of basins whose slope angle would have been enough to produce solifluction deposits or trap glacial sediment. However, the unsorted nature of the material does not favour a process of sedimentation in a small lake at Cefn Mawr in the early Holocene.

The accumulated organic material is very well humified below 125 cm, and below 257 cm contains frequent wood fragments, mainly of *Betula* and *Alnus* (fig. 6.19). It is likely, therefore, that these species were growing in the immediate vicinity of the bog. It is interesting to note that these wood fragments disappear from the core at the same time as the main decline in these species occurs in the pollen record, suggesting that the loss of tree cover occurred simultaneously across the whole landscape (fig. 6.19 and Appendix IVd).

Local pollen assemblage zone (LPAZ) CM1a is represented by the period 6,175±50 years BP (SRR-5056) to 4,520±50 years BP (SRR-5055), giving an accumulation rate of 64.9yrs/cm (fig. 6.24). Peat accumulation began in a period when *Sphagnum* spores were dominant, along with grass and shrub pollen. The high percentage of *Sphagnum* spores at the base of the organic core section (25%) possibly represents a degradation of other pollen types since *Sphagnum* spores have been shown to be relatively resistant to decay. Total tree pollen values rise very rapidly across the minerogenic/organic sediment boundary, due mainly to an increase in the levels of *Alnus* and *Pinus*. This may represent the "alder rise" as referred to by Chambers and Price (1985). However, the date for this at comparable sites in North Wales is given as around 8,000 BP, and as such it is not likely that this rise is related to an immigration of *Alnus* into the area. *Alnus* pollen levels can be seen to fluctuate quite considerably, between 80% and 20%, and the rise shown at the base of this diagram probably indicates one such fluctuation. Such fluctuations are also noted in the pollen concentration diagram.

This is coupled with an absence of detectable levels of pollen in the underlying minerogenic sediment, resulting in higher values for the more recalcitrant palynomorphs, such as *Sphagnum*. *Pinus* pollen values also decline quite sharply across this boundary, another indication that these changes may be more a result of the sedimentation regime rather than actual vegetation changes. By the top of CM1a tree pollen values reach 80%, the landscape being dominated by trees and shrubs, with very low proportions of grasses and other herbs. It is thought (Lynch, 1993) that the reason the uplands were inhabited by man during this period was because of a better climate and the existence of a less dense woodland cover, allowing easier clearance and movement. It is, however, difficult to establish vegetation densities from pollen diagrams due to uncertainties over the pollen source area. It is possible that tree pollen from denser valley woodlands may be masking the more open character of the upland woodlands. This is possible since both *Ulmus* and *Quercus* are components of the pollen diagram whilst it is more likely that they were growing at lower altitudes.

Throughout CM1b tree and shrub pollen percentages remain high, although four main fluctuations occur, usually resulting from a reduction in tree pollen and an associated increase in shrub pollen, with two phases of an increase in herb pollen, mainly Gramineae and Cyperaceae species. These four increases in shrub pollen, all relating to an expansion of *Salix* and *Corylus* pollen, are noted in both the pollen percentage and pollen concentration diagrams. They occur at 365 cm, 355 cm, 329 cm and 317.5

cm between $4,520 \pm 50$ years BP (SRR-5056) and $4,475 \pm 50$ years BP (SRR-5054). These would seem to relate to wetter episodes during this period with a loss of *Alnus* and *Betula*, being replaced by *Salix*, although there are no peaks in aquatic pollen at these points to suggest wetter phases.

However, *Sphagnum* spore frequencies do increase at these points, both in pollen percentage and pollen concentration diagrams, which suggests that the surface of the peat bog or areas prone to waterlogging in the surrounding landscape had become wetter. Some other herbs also show higher levels at these points, such as *Filipendula* and *Compositae (tub)*, which may mean that these changes simply represent the increased penetration of light through the canopy and an increase in the ground flora. Increases in rain intensity at the soil surface due to a loss or reduction in the protective woodland canopy may have led to the temporarily increased wetness in some sites prone to waterlogging and thus explain the increase in *Sphagnum* spores at these points.

The cause of this may be the early activities of man at this site, or at least in this region, where small openings were created and subsequently abandoned and into which shrubs moved and colonised prior to re-invasion by tree species. This is suggested by the increase in grass pollen during three of these phases, along with an increase in *Filicales* spores, which may represent an opening up of the forest canopy. This is highlighted by the case of *Corylus*. It has been shown (Hibbert, 1993) that *Corylus* can form a major part of the understorey of woodlands, but produce little pollen due to low light levels, and only show up clearly in the pollen record when the canopy of the woodland is disturbed allowing more light to penetrate to the understorey. The relatively low values for *Corylus* throughout this pollen sequence compared with other pollen records for the area (Hibbert, 1993) may therefore not actually reflect the true amount of this species if it was growing as an understorey in a fairly dense woodland with its propensity to flower diminished (Faegri and Iversen, 1989). The *Corylus* peaks may indicate a break-up of the forest canopy.

From the above discussion it is obvious that it is very difficult, simply from pollen data, to distinguish between natural vegetation changes and changes brought about by man, especially when the levels of activity must have been fairly low. Webb (1994) suggested that if the disturbance of vegetation by the first agricultural peoples were at the same intensity as natural disturbances, then such people could be present and active but be largely undetectable by analysis of pollen data from lakes and bogs, which typically have a pollen source area of 100-1000 km² or more.

It is, therefore, difficult to come to a definite conclusion as to the cause of the fluctuations in the vegetation community during CM1b. Zones CM1a and CM1b, which both include records of the presence of fire in this landscape, cover the Mesolithic period when, from archaeological evidence, Quinnell *et al.* (1994) suggested that the site at Aled Isaf was occupied. They suggested that this site was only used as a summer hunting camp but even so, if fire was being used to clear land or drive game, this could well have set in motion some of the changes noted. This is further suggested by the fact that three of the four increases in shrub pollen are related to losses of *Ulmus* pollen at this site. There is no clear evidence for an elm decline here, and this is a similar situation to that described by Hibbert (1993) in the Brenig Valley, who suggested that this was due to elm pollen being blown up from the valleys and so not registering very well in the pollen diagram. If elm leaves were being used in the lower valleys for fodder resulting in an increase in shrub pollen due to increased light penetration of the canopy, then this may explain these fluctuations and suggest that a proportion of the pollen recorded at this site has a regional origin.

An analysis of charcoal concentrations in the peat from Cefn Mawr hints at a human influence on the vegetation during CM1b (fig. 6.21). Charcoal concentration peaks 4 times, three of which correspond with low tree pollen values, indicating that when clearance did occur there were fires in the region, suggesting that the vegetation changes noted were brought about by human activity. However, as noted in section 4.3, there are many problems involved in the interpretation of charcoal concentration data. It is possible that these peaks in charcoal represent either deliberate clearance of the woodland, or natural fires occurring across the landscape. It is equally possible that the fires were occurring close to the site or some distance from Cefn Mawr, but in the case of the latter, they would have to have been more extensive. However, throughout CM1c there is little fluctuation in tree pollen and little charcoal present in the core, which may indicate that these fires were not natural and were caused by the people present at this site during this period.

Comparison of CM1b and CM1c highlights some obvious differences which, as previously noted, may help to solve some of the problems outlined above. Zone CM1c is the period 4,475±50 years BP (SRR-5054) to 3,530±55 years BP (SRR-5052), and is marked by a comparatively stable woodland component at ≈80%, with little variation in either shrub or herb pollen. Fluctuations in the composition of the woodland do occur, but overall quantities of tree pollen remain constant. The main difference is evident in the response of the shrubs. Both *Corylus* and *Salix* pollen

show a sudden decline, at the base of CM1c, seen in both the percentage pollen and pollen concentration diagrams, with associated peaks of spores, excluding *Sphagnum*. This is suggestive of a drying out of the site with a subsequent loss of aquatic species and a more stable woodland environment. There is also an increase of *Ulmus* pollen at this point.

This "stability" of the vegetation community may have been due to a cessation of human activity, a fact which is backed up by a lack of archaeological evidence relating to this period (Dr J. Williams, pers. comm.), if this were the cause of the fluctuations during the previous phase. The species change is suggestive of a drier period, with a reduction in *Salix* and *Corylus* pollen and *Sphagnum* spores. However, a drying out of the site would not necessarily result in a movement of people away from the area, and so the reduction in disturbance of the vegetation community may be due to some other reason, or to a movement of the population away from the area for some reason other than the environmental conditions of the site.

This pattern, therefore, seems to suggest that CM1 was influenced by alternating periods of wetness and dryness causing alterations in the vegetation community. There is, however, no indication of this in the core stratigraphy. This CM1 period does mark the transition from the Atlantic to the Sub-Boreal climatic period, and this would be consistent with the data presented here, which indicates a shift to a warmer and drier climatic phase. It seems, therefore, that the major variations in the vegetation community noted throughout CM1b and CM1a were climatically induced with human activity possibly occurring, but at a level not always clearly detectable from these pollen data. One point to note concerning the dating of CM1 is the seemingly anomalous accumulation rate of 0.71yrs/cm between the two dates SRR-5055 (4520±50 years BP) and SRR-5054 (4475±50 years BP). The depth-age profile indicates that the former may be too young, but it is not clear what the reason for this may be since it is not thought that there was any contamination of these lower samples by young carbon during the sampling and handling stages.

The most noticeable change in this pollen diagram occurs during LPAZ CM2. This zone covers the period 3,530±55 years BP (SRR-5052) to 2,805±50 years BP (SRR-5050) and is marked by a shift to a much more open landscape. At the base of this zone tree pollen values total around 80%, but by 3,515±50 years BP (SRR-5051) this level has fallen to around 45% along with a reduction in shrub pollen. Between 3,515±50 years BP (SRR-5051) and 2,805±50 years BP (SRR-5050) levels of tree and shrub pollen remain fairly constant. The main loss of tree pollen is due to reductions

in *Betula* and *Alnus* pollen, which are replaced by pollen from Gramineae species. The lower boundary of this zone also shows a peak of *Nuphar* pollen and a reduction of Filicales and *Polypodium* spores, with a slight increase in *Sphagnum* spore frequencies. This again gives the impression of a wetting of the climate although, since no increase in *Salix* or *Corylus* pollen is noted, it is possible that the opening up of the woodland allowed more light to reach streams and other watercourses so allowing an increase in the flowering potential of aquatic species; the loss of ferns would simply reflect the reduction in the woodland component.

Gramineae species are the main beneficiaries of this initial loss of woodland cover, and *Rumex* pollen also shows peaks during this phase. The main problem here is to know what the cause of this change was. Increased aquatics indicate a wetter environment at the lower boundary of CM2, and the only change noted in the stratigraphy at this point is a loss of wood fragments from the core, suggesting that the reduction in tree pollen was due, in part, to the loss of woodland cover in the immediate vicinity of the bog.

However, the fact that the decline in tree pollen and subsequent levelling off of the curve (fig. 6.21) is so sudden suggests a more dramatic cause, possibly man. This is a period when it is thought (Lynch, 1993) that the population in Clwyd and N. Wales as a whole was increasing, and it is also a period when mining activity in areas such as the Great Orme on the North Wales coast is thought to have been intense, requiring a large supply of wood to be converted into charcoal for the firesetting and smelting process. This use of wood could have involved coppicing, which would have reduced the flowering capacity of trees, which may explain the sudden decline followed by the levelling off of pollen percentages. However, of the stumps exposed around the margins of Aled Isaf none show signs of coppicing, and this would suggest that if coppicing was the case then the practice was taking place in the lower, more accessible, valleys. It is not likely that mining activity on the coast would have used wood from Hiraethog, and thus it may be that this vegetation change evident at Cefn Mawr is regional in nature.

A further indication of the probable role of man in the changes noted during CM2 is the increase in charcoal concentration at the base of CM2, with three peaks in charcoal being noted. This again indicates the occurrence of fire in the region, and it is likely that this was caused by man since, as described earlier, little charcoal was found in the preceding LPAZ CM1c: if the fires suggested by these data were caused naturally it might be expected that they would be recorded throughout the core. Also,

if the lower boundary of CM1c were to mark a drying of the climate, then, if the fires were natural, it would be expected that this zone would have registered an increase in the charcoal concentration recorded.

Zone CM3 is characterised by a further, gradual decline in total tree pollen, with some initial fluctuations, and a replacement of Gramineae species by *Calluna* pollen. CM3a, whose lower boundary has been dated to 2,805±50 years BP (SRR-5050), shows an overall decline in total tree pollen, although this includes several fluctuations, along with a high, but fluctuating Gramineae pollen percentage and a gradually increasing *Calluna* pollen percentage. This is also marked by a slowly increasing *Sphagnum* spore percentage which shows a sudden peak at the boundary between CM3a and CM3b. The ¹⁴C dates place this zone in the Bronze Age, and Hibbert (1993) suggested that during the Bronze Age fields were being cut out of the heather to improve grazing. The fluctuating Gramineae values may represent this, especially as some peaks coincide with those for Caryophyllaceae, herbs indicative of pasture. The fluctuating total tree values may also represent attempts to bring more land into grazing, especially in the uplands, since the decline is attributed almost entirely to a decline in *Betula* pollen. Fire may also have been a cause, possibly in its use to control the initial spread of heather over the uplands. This is indicated by the peaks noted throughout this zone in charcoal concentration. These coincide with the fluctuations in woodland and indicate that fire was a factor of the environment of Hiraethog during this period and that it may have been used by Man in the management of the vegetation, possibly in the control of heather since low *Calluna* pollen values coincide with higher charcoal concentrations.

Zone CM3b shows a continued steady decline in total tree pollen, with little variation in the total shrub pollen over this period. It also marks the beginning of a shift from Gramineae species to *Calluna* and Cyperaceae, along with an increase in *Sphagnum* spores. *Plantago* pollen first appeared during zone CM3a, but shows a marked increase in zone CM3b. *Plantago* is commonly considered to be an anthropogenic indicator species (Behre, 1986), indicating the agricultural activities of man in an area. *Rumex* is another species commonly used in this context. However, *Rumex* pollen shows its greatest change at the base of CM2 when the sudden loss of tree cover occurred, whereas when *Plantago* pollen appears *Rumex* pollen begins to tail off. Behre(1986), who suggested the use of an arable/pasture index, suggested that the presence of *Plantago*, *Rumex* and members of the Chenopodiaceae family together were indicative of pasture rather than an arable system, and Chenopodiaceae clearly show larger peaks throughout CM3 than in previous zones. This would

suggest that over the later Holocene the Hiraethog Moors have served as mainly grazing areas. No indication of cereal pollen was noted in any samples, but this does not rule out a more arable-based land-use in the lower valleys.

The idea of pastoral land-use through zone CM3 is further backed up by the fact that several Gramineae peaks coincide with Chenopodiaceae peaks. From analysis of peats and buried turves in the Brenig Valley, Hibbert (1993) suggested that, during the Bronze Age and Iron Age, fields were being cut out of the heather moorland to improve grazing, and these features in the pollen record from Cefn Mawr may be a further indication of this practice. This may also explain some of the fluctuations which occur in the pollen values for *Calluna* over this period.

The marked peak in *Sphagnum* spores at the base of CM3b is suggestive of an increased wetness, as is the increase in Cyperaceae and *Calluna* and the decline in all tree species at this point. This lower boundary is dated to approximately 2,060 years BP, which relates to the climatic boundary between the Sub-Boreal and Sub-Atlantic and the shift to a cooler and wetter climate. This would explain the change in the vegetation types noted at this point.

The relative stability in the overall vegetation recorded in the pollen diagram during CM3b possibly relates to the Dark Ages in Clwyd which occurred over this time period (Edwards, 1991). Little archaeological evidence is available for this period, although it is suggested that the presence of the powerful kingdom of Gwynedd to the west and increasing Anglo-Saxon penetration from the east may have meant there was little opportunity for the emergence of any strong regional identity in Clwyd. This may have led to a fairly stable population and consequently a constant land-use practice throughout the area.

During the following Medieval period (928-544 BP) Jones (1991) suggested that the uplands of Clwyd were used extensively for grazing, and this would have maintained the grass/heather vegetation community already present. As a possible example of this is cited the commote of Ceinmeirch where the waste of Bishopswell, adjoining the boundary of Cernenfed, contained an area of 580 hectares at an altitude of over 300m. In 1334 it was estimated that this pasture could sustain 8 bulls and 192 cows in winter as well as in summer, and have sufficient hay for the sustenance of all these animals in winter. It is suggested also that this system was in use well before the Edwardian Conquest (Jones, 1991).

Towards the top of the core, from 395±45 years BP to the present day, total tree pollen and shrub pollen values begin to fluctuate more. Increases in shrub pollen are due to *Corylus* and *Salix* pollen, and *Plantago* pollen settles at a higher value than before. These changes possibly relate to a more sustained agricultural (pastoral) use of the land, and to further woodland clearances as industrial activities became more intense up to and during the industrial revolution. At around 140 years BP there is a sharp decline in woodland with a total loss of shrubs, and this may relate to a more intense industrial phase, coinciding perhaps with an increase in mining and metal working in the east of Clwyd as well as local mining at Llansannan (Greuter and Lloyd Williams, 1991). *Sphagnum* spores again rise at the top of the core, which may relate to a further wetting of the climate or, at least, of the bog surface. Throughout CM3b charcoal is present, and shows several peaks. These represent the continued occurrence of fire in this environment, although in this more open landscape it is possible that charcoal fragments could have originated further from the site of deposition. Three such peaks coincide with low *Calluna* pollen values, and may indicate a use of fire to control the encroachment of heather across the existing pastures.

Present-day land uses include sheep grazing, coniferous plantations and water management. In the recent past Hiraethog has been managed as a grouse moorland by the burning of heather, and such practices will help maintain the heathland vegetation community and prevent tree species from re-colonising the area.

6.9.2 Llyn y Foel-frech, Hiraethog.

6.9.2.1 Results

The core retrieved from Llyn y Foel-frech was 340cm in length and came from the deepest part of the lake, under 450±25cm of water. The top 30cm of sediment was too waterlogged to collect. At 216cm from the top of the core was a sharp transition from a dark organic-rich sediment to a light grey inorganic sediment.

Figure 6.25. Llyn y Foel-frech water depth (m).

x = coring location

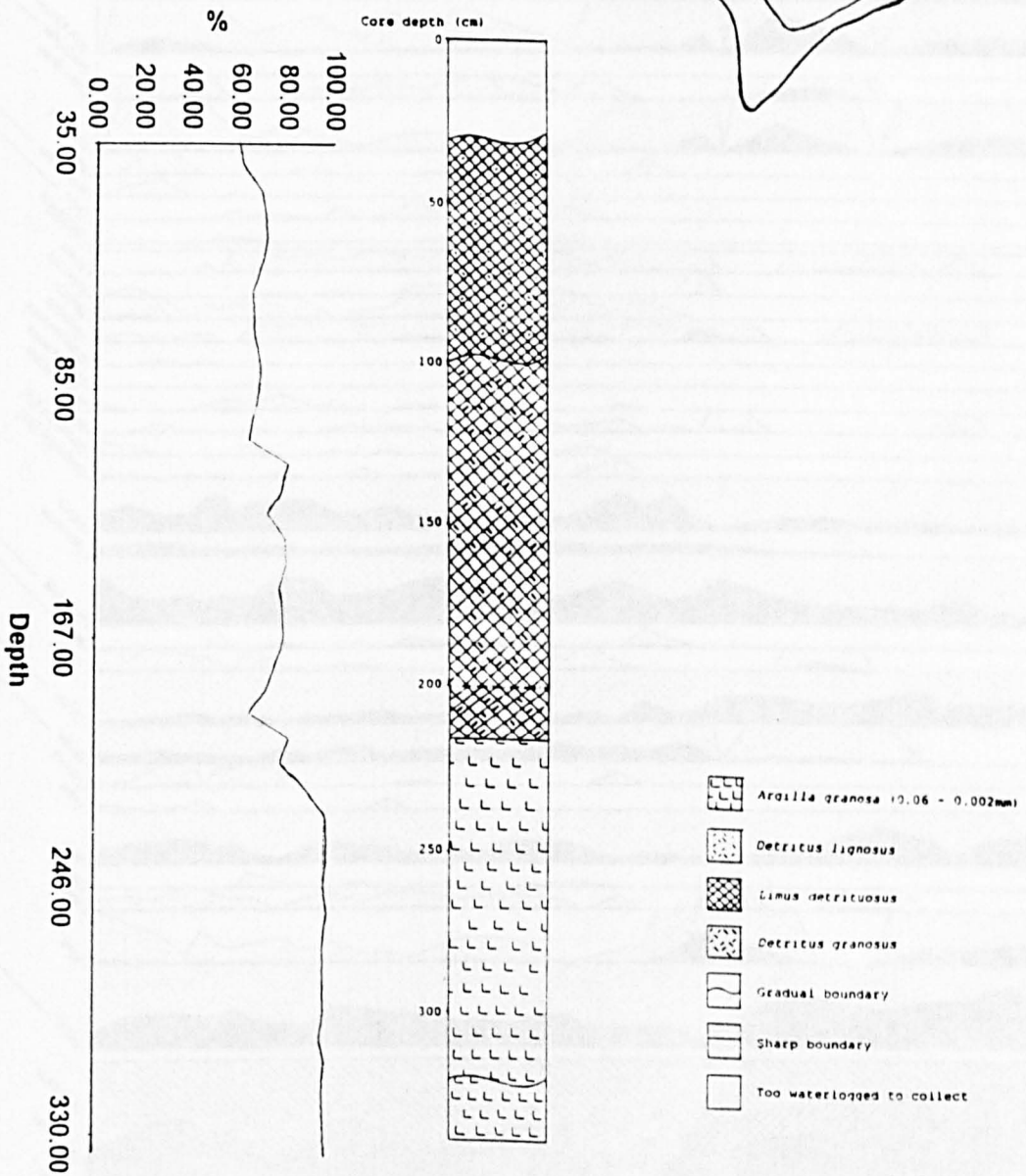
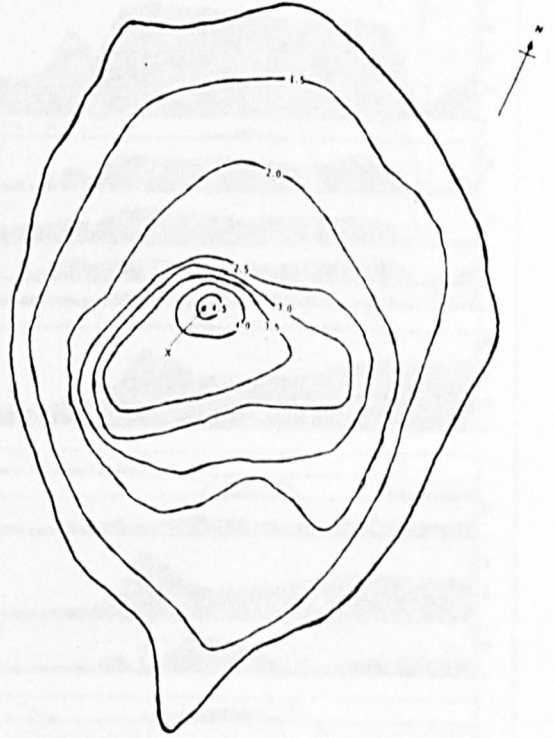


Figure 6.26 Llyn y Foel-frech core stratigraphy and loss-on-ignition (ash content) data.

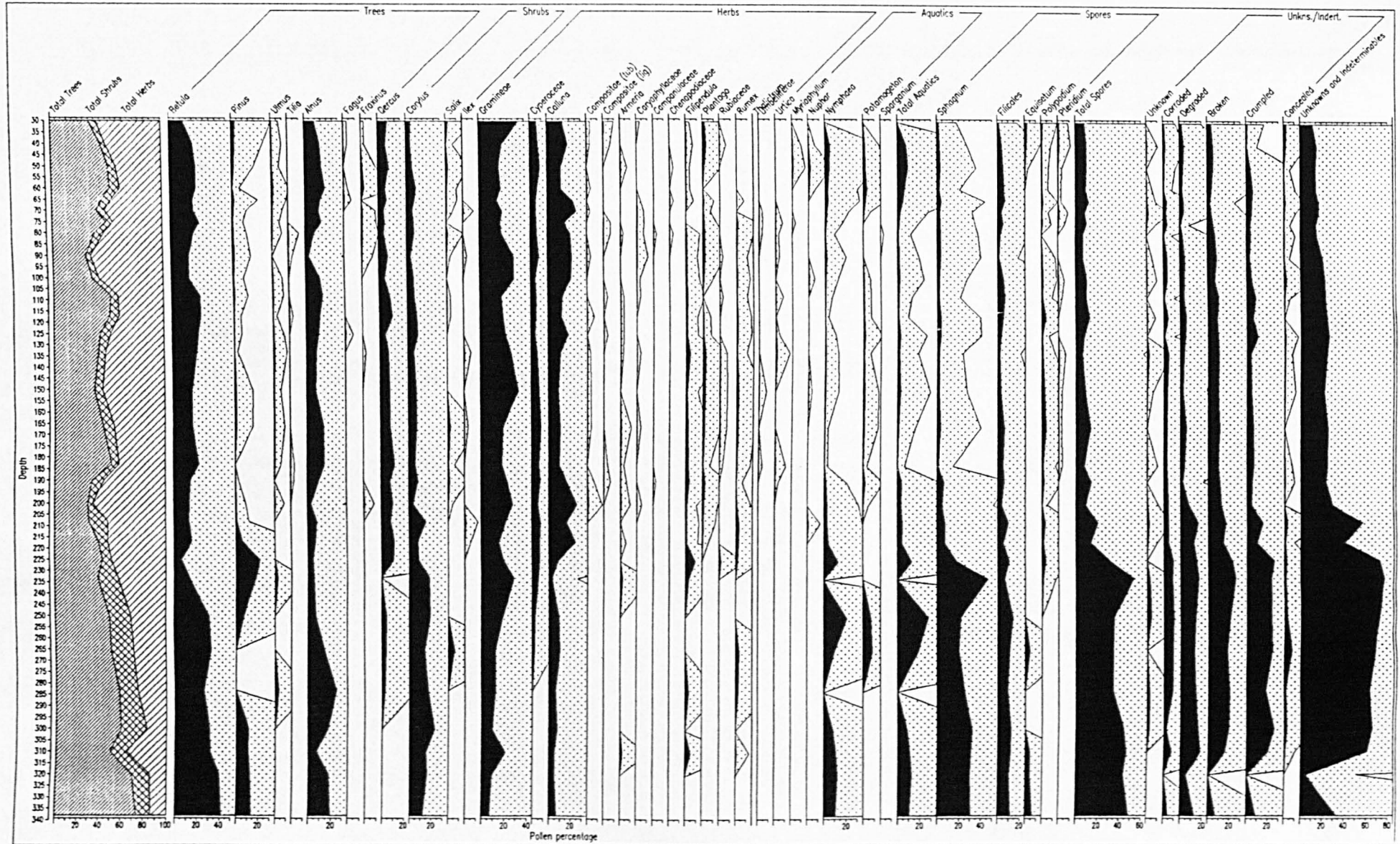


Figure 6.27 Llyn y Foel-frech pollen percentage diagram.

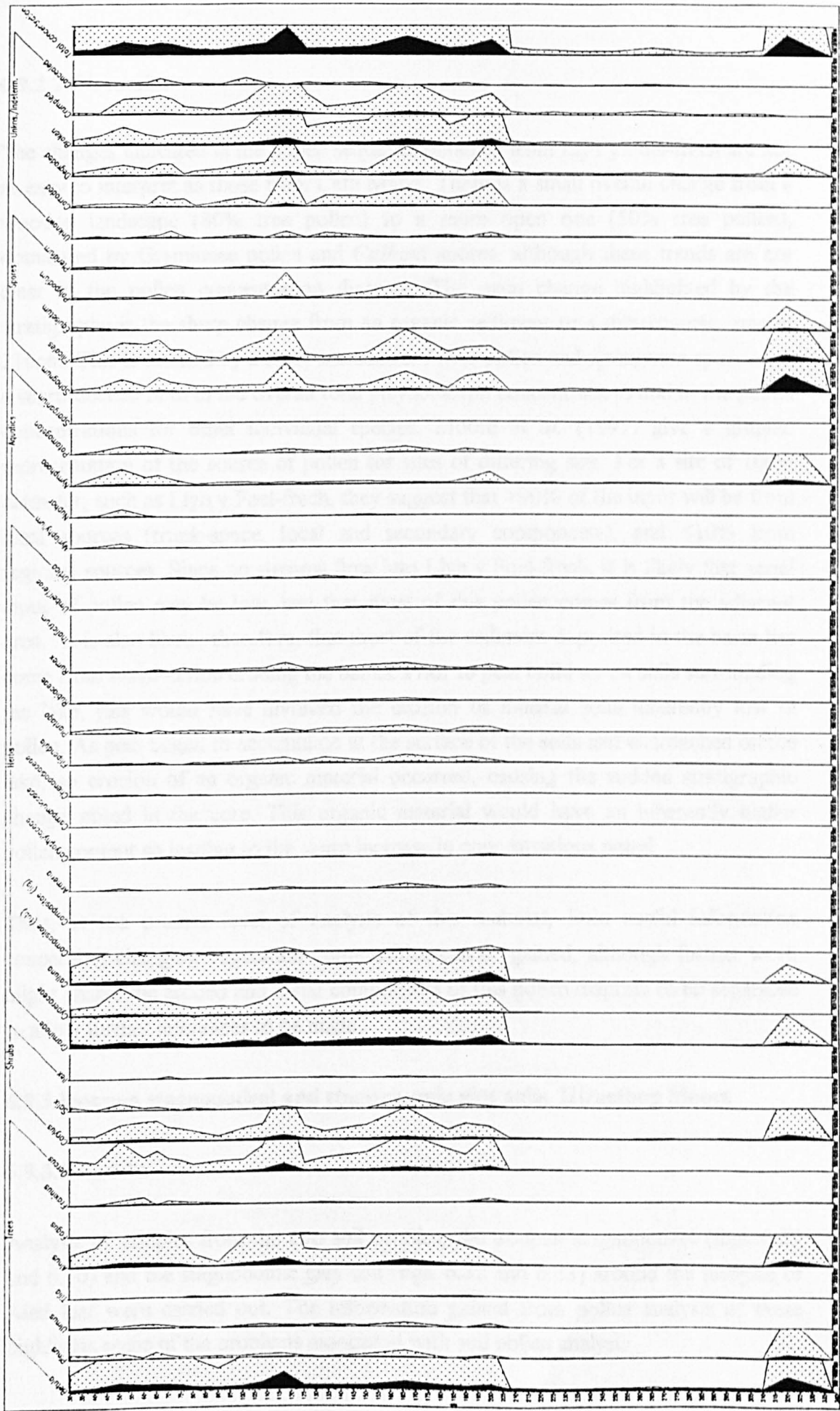


Figure 6.28 Llyn y Foel-frech pollen concentration diagram.

6.9.2.2 Discussion

The changes indicated in the pollen sequence obtained from Llyn y Foel-frech are not as easy to interpret as those from Cefn Mawr. There is a small overall change from a wooded landscape (80% tree pollen) to a more open one (50% tree pollen), dominated by Gramineae pollen and *Calluna* spores, although these trends are not clear in the pollen concentration diagram. The main change highlighted by the stratigraphy is the sharp change from an organic sediment to a minerogenic one at 216cm. This is marked by a sharp increase in *Pinus* pollen and *Sphagnum* spores and a sharp decline both in the overall total palynomorph concentrations and in the pollen concentrations for other individual species. Moore *et al.* (1991) give a graphic representation of the source of pollen for sites of differing size. For a site of 100m diameter, such as Llyn y Foel-frech, they suggest that >90% of the input will be from local sources (trunk-space, local and secondary components), and <10% from regional sources. Since no streams flow into Llyn y Foel-frech, it is likely that aerial input of pollen may be low, and that most of this pollen comes from the adjacent area. It is also likely, therefore, that most of the sediment deposited in the basin has come from wave-action eroding the banks. Prior to peat build up on soils surrounding the lake, this would have involved the erosion of mineral soils inherently low in pollen. As peat began to accumulate at the surface of the soils and encroached on the lake, so erosion of an organic material occurred, causing the sudden stratigraphic change noted in the core. This organic material would have an inherently higher pollen content so leading to the sharp increase in concentrations noted.

Thus, at the present level of analysis of this material, little useful information concerning changing vegetation communities can be gained, although further work might enable the eroded and aerial components of this pollen diagram to be separated to allow further inferences to be made.

6.9.3 Ironpan stagnopodzol and staghomic gley soils, Hiraethog Moors

6.9.3.1 Results

Analysis of samples from the two soil profiles, the ironpan stagnopodzol (figs. 6.29 and 6.30) and the staghomic gley soil (figs. 6.32 and 6.33) around the margins of Aled Isaf were carried out. The information gained from pollen analysis of these highlights some of the problems associated with soil pollen analysis.

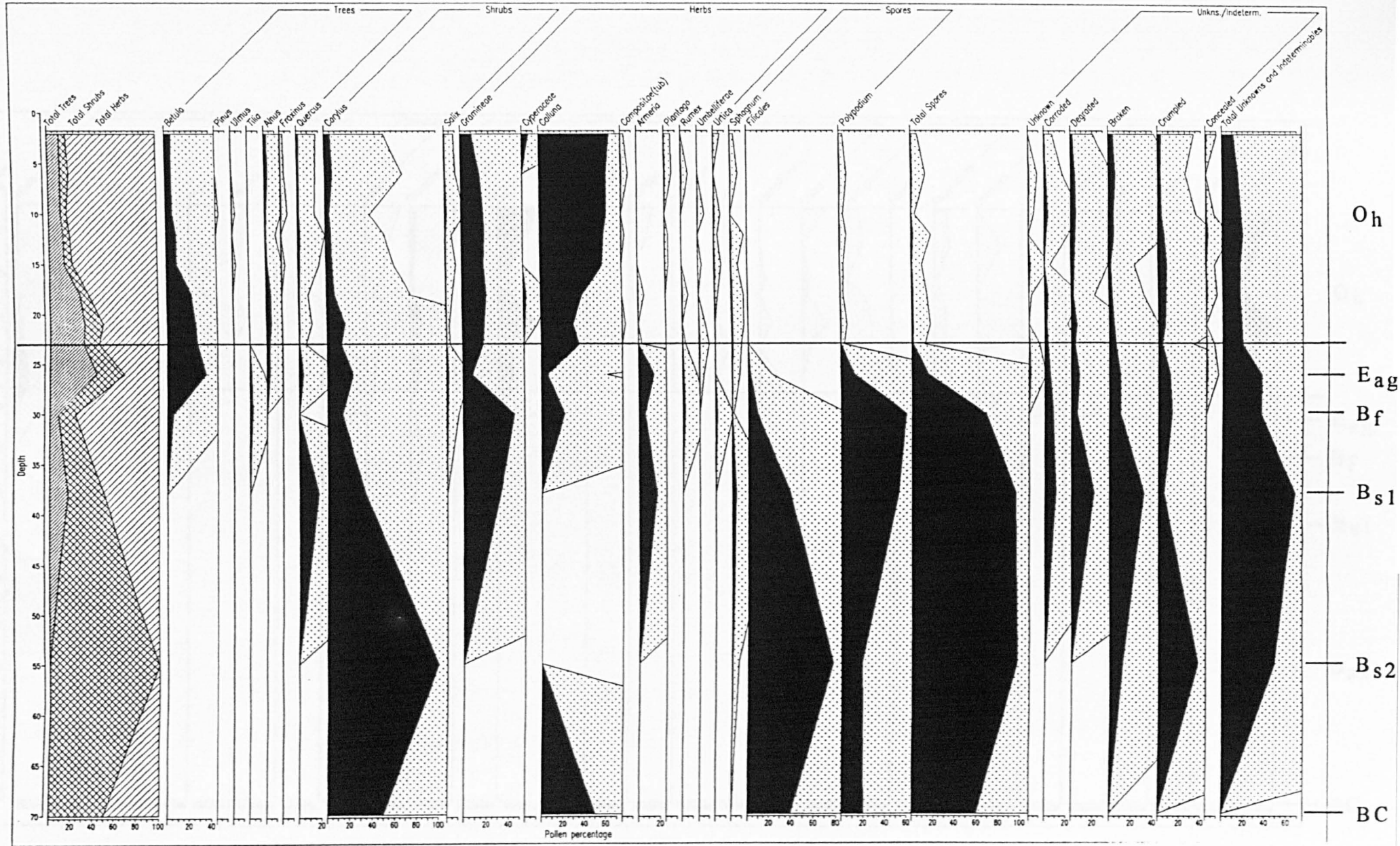


Figure 6.29 Ironpan stagnopodzolic soil pollen percentages.

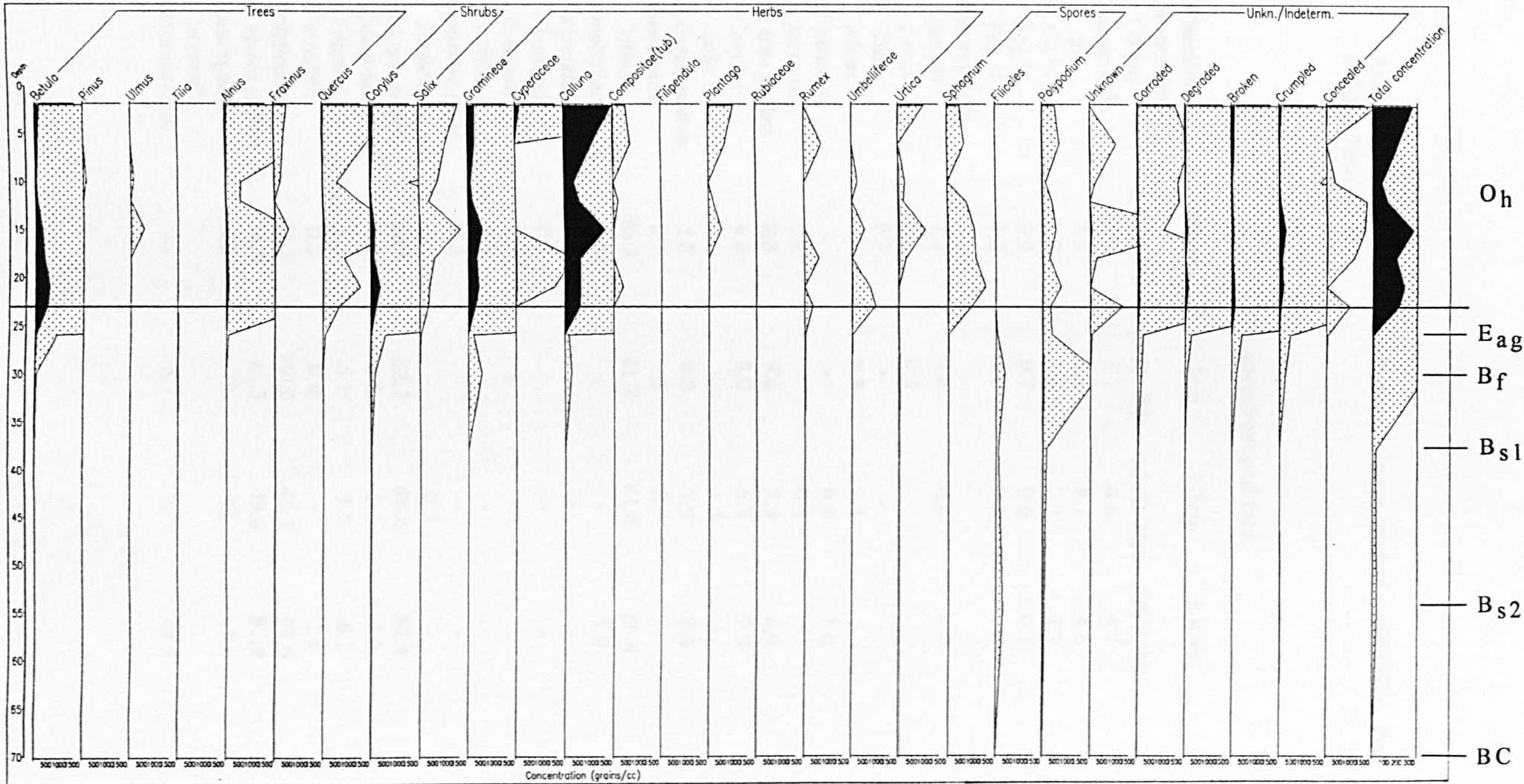
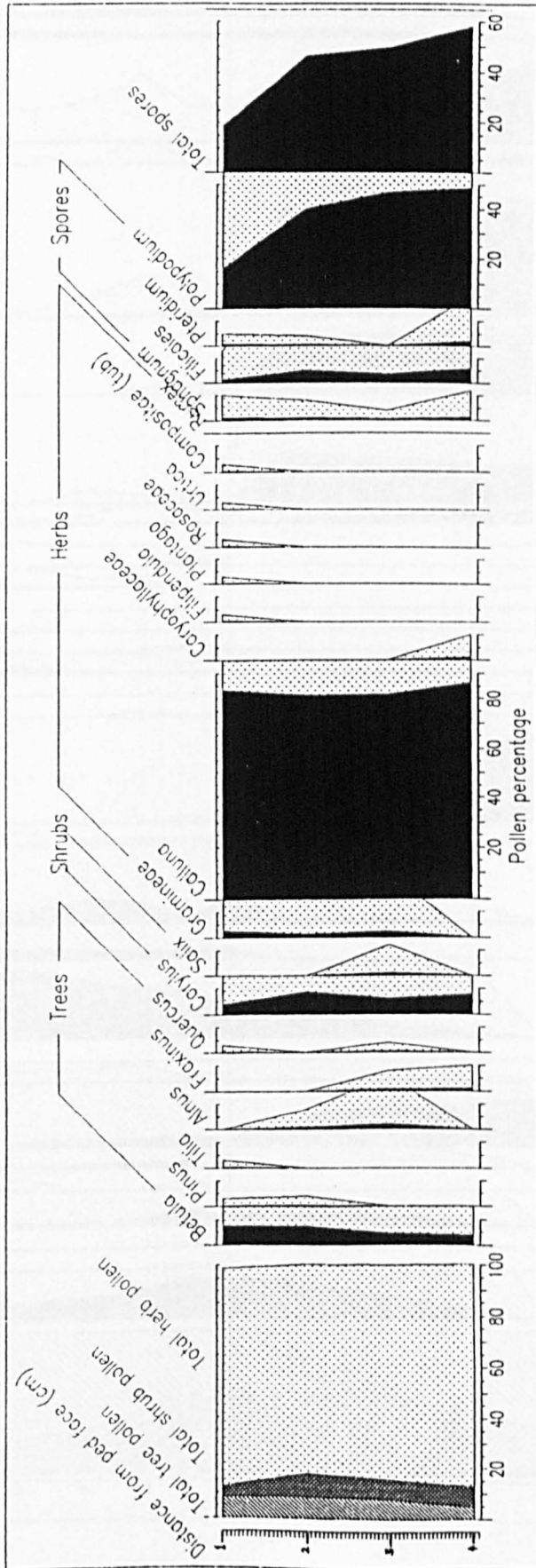


Figure 6.30 Ironpan stagnopodzolic soil pollen concentrations.

Table 6.9 Analysis of an E_{ag} ped from the ironpan stagnopodzol profile (P2). Ped width is 7cm.

Chemical properties	Distance from ped face.			
	0-1cm	1-2cm	2-3cm	3-4cm
Colour	2.5YR 3/0	10YR 7/2	10YR 7/2	10YR 7/2
Organic C %	6.3	5.1	4.6	4.7
pH	3.9	4.1	4.1	4.1
C _p %	2.7	2.6	2.3	2.3
Fe _p %	0.9	0.7	0.6	0.7
Fe _d %	1.2	1.0	0.9	1.0
Pollen types %				
<i>Betula</i>	7.4	7.4	4.6	3.9
<i>Pinus</i>	0.3	0.4	-	-
<i>Tilia</i>	0.3	-	-	-
<i>Alnus</i>	-	0.8	2.1	-
<i>Fraxinus</i>	-	-	0.8	1.0
<i>Quercus</i>	0.3	-	0.4	-
Total tree pollen	8.3	8.6	7.9	4.9
<i>Corylus</i>	4.0	8.8	6.3	7.8
<i>Salix</i>	-	-	1.2	-
Total shrub pollen	4.0	8.8	7.5	7.8
Gramineae	2.7	1.5	2.5	-
<i>Calluna</i>	83.3	81.2	81.6	86.4
Caryophyllaceae	-	-	-	1.0
<i>Filipendula</i>	0.3	-	-	-
<i>Plantago</i>	0.3	-	-	-
<i>Rosaceae</i>	0.3	-	-	-
<i>Urtica</i>	0.3	-	-	-
<i>Compositae (tub)</i>	0.3	-	-	-
<i>Rumex</i>	-	-	0.3	-
Total herb pollen	86.5	82.7	84.4	87.4
<i>Sphagnum</i>	1.0	0.8	0.4	1.2
Filicales	1.3	5.1	3.5	6.1
<i>Pteridium</i>	0.5	0.4	-	2.0
<i>Polypodium</i>	16.1	40.0	46.7	48.6
Total spore pollen	18.9	46.3	49.6	57.9
Total species present	16	10	12	9
Indeterminables	4.2	8.7	9.5	13.4

Figure 6.31 Pollen percentage diagram for a ped from the E_{ag} horizon of a stagnopodzolic profile



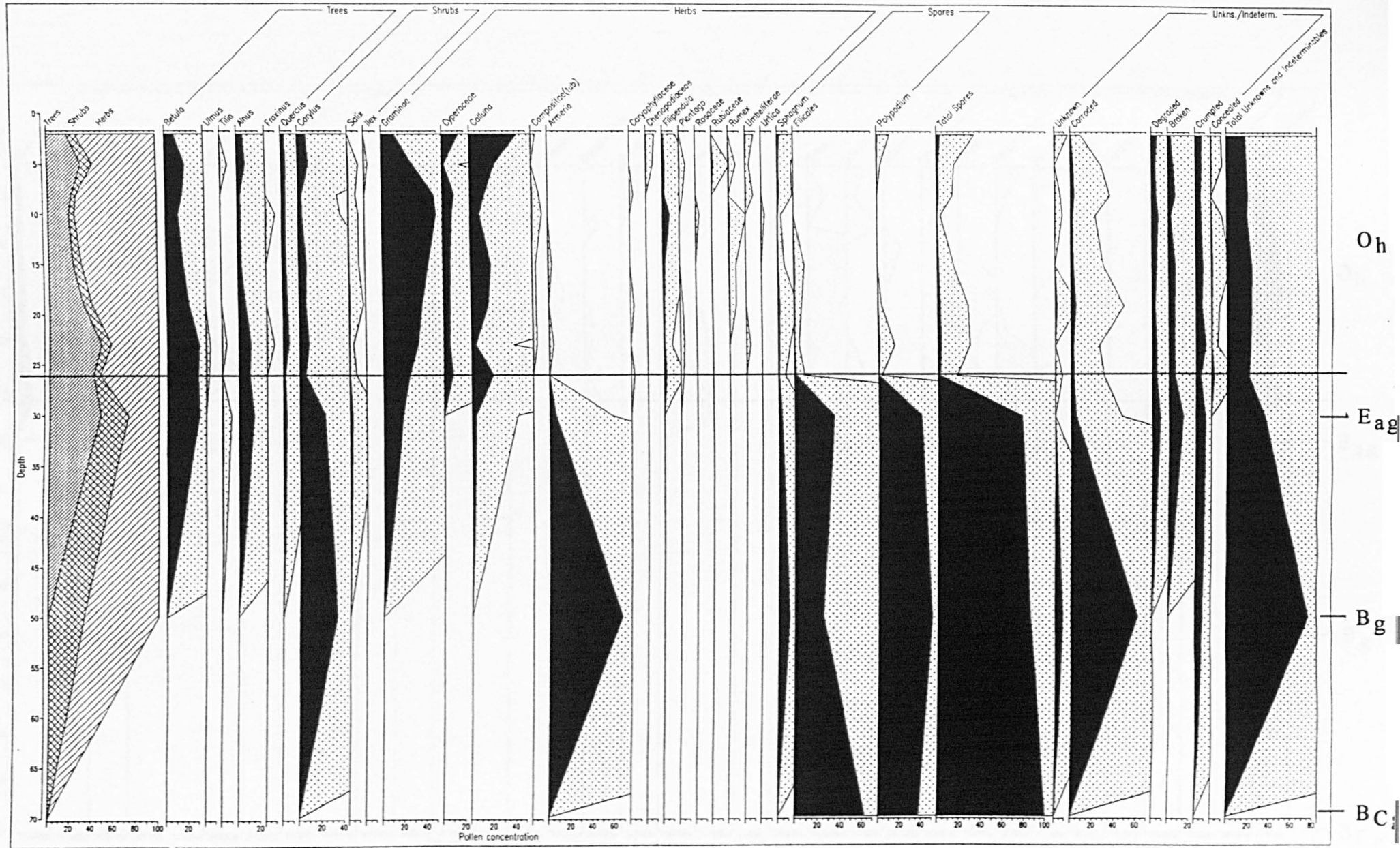


Figure 6.32 Stagnohumic gley soil pollen percentages.

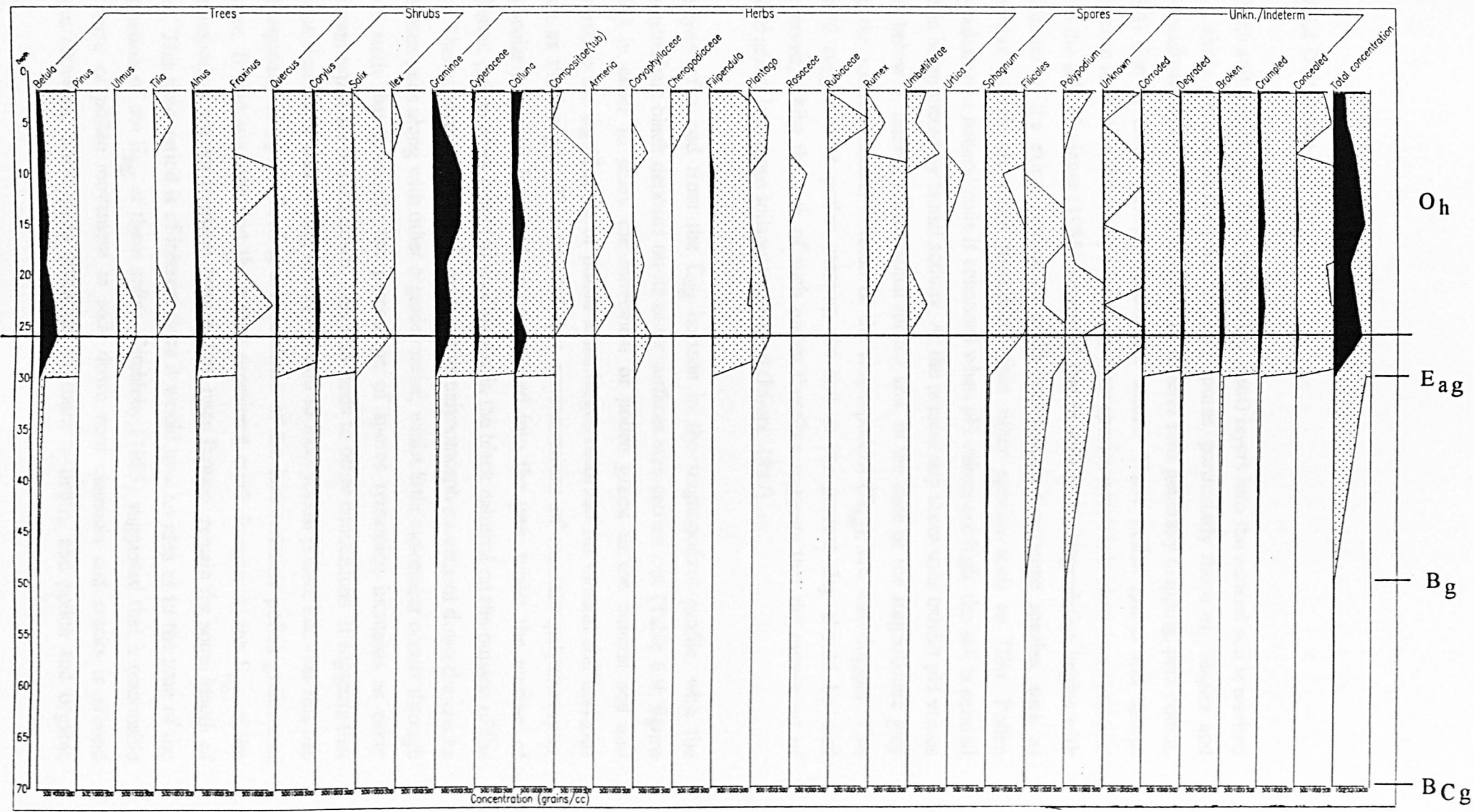


Figure 6.33 Stagnohumic gley soil pollen concentrations.

6.8.3.2 Discussion

In both soils the change from surface O_h (peat) layers into the mineral soil is marked by a sharp increase in the percentage of spores, particularly those of Filicales and *Polypodium*, which are characteristic of mineral soils generally (Tipping, pers comm, 1994) due to their relatively recalcitrant nature. These pollen grains and spores therefore increase relative to pollen from other species which is broken down and lost from the soil. Havinger (1985) suggested that in soils pollen degradation begins with oxidation of the exine, leading to under-representation of some species, such as *Quercus*, which are more susceptible than other species such as *Tilia*. Pollen degradation in mineral soils is enhanced when pH values are high, the soil is aerated and is being mixed by faunal activity. At the present day these soils exhibit pH values well below 5, undergo little faunal mixing and, in the case of the stagnohumic gley and the surface mineral horizon of the stagnopodzol (E_{ag}), are waterlogged. This would suggest that pollen entering the soil at the present day should be well preserved, whilst the lack of such pollen therefore suggests that the movement of pollen grains into these soils was restricted (Miura, 1987).

Analysis of a ped from the E_{ag} horizon in the stagnopodzol profile, with the characteristic black deposits on its outer surfaces was carried out (Table 6.9; figure 6.31) in order to study the movement of pollen grains in the mineral soil and determine the significance of pollen assemblages recorded for mineral soil horizons such as the ironpan. This showed that concentrations of resistant palynomorphs, particularly spores, increased as one moved into the ped, whilst the number of different pollen types recorded was highest in the black material on the outside of the ped. This confirms that there is more active palynomorph movement down the cracks between peds along with other organic matter, whilst little movement occurs through peds such that gradually the percentage of spores remaining increases as other palynomorphs are broken down. This also leads to other conclusions. It suggests that at one time there was mixing of this horizon to incorporate pollen, and that this has subsequently stopped allowing a breakdown of the less resistant pollen grains and spores. It also suggests that these very prominent crack features in the E_{ag} of the stagnopodzol are not transient features but, once formed, remain for some length of time. This time period is of interest since it would give an idea as to the time of the formation of the E_{ag} of these soils. Dimbleby (1985) suggested that a reasonable estimate of pollen movement in soils down root channels and cracks is around 10cm/300years. These peds occur up to 10cm in depth, and pollen and organic

matter were present at the base of cracks running vertically through them. This would suggest that these cracks may have persisted for several 100 years, although since spore concentrations were higher on the ped surfaces than in the overlying peat, this may mean that they have been present for longer to allow degradation of some pollen types to occur. It is, however, difficult to make further inferences concerning vegetation changes based on the pollen analytical data of mineral soil horizons.

It has also been suggested that the pollen composition of material accumulating above an ironpan (Bf) can be used to supply information on the timing of ironpan development, especially if the cracks described above run down to the pan. The data for this profile (figure 6.32) indicates a grassland/heather vegetation since the ironpan formed and that ironpan development occurred following the removal of woodland cover. However, the sample of Bf analysed also showed a high percentage of spores, which may indicate that the full pollen assemblage is not present; the palynomorphs found having been washed down the profile and trapped by the placic horizon at a rate such that degradation of some of the less resistant grains has occurred.

Surface organic deposits in these soils are built up stratigraphically in a strict temporal order without faunal disturbance and as such can be useful for palynological studies. Both profiles show that peat accumulation began as *Calluna* pollen begins to increase sharply with, in the stagnopodzol profile, a decline in *Betula* and Gramineae species. At the stagnogley site tree pollen also declines, but there is an increase in Gramineae pollen associated with the *Calluna* rise. This may simply reflect the vegetation community which has a large component of *Molinia* in these wetter areas. These results confirm the assumption that peat development is associated with vegetation types which produce a litter less easily degraded, and that grow in more acidic conditions, also reducing organic matter breakdown. This would possibly place peat initiation in these soils in LPAZ CM3b. Dates available for peat initiation at this site (Avery, 1990; section 6.5) are $580 \pm ?$ years BP and $1,2656 \pm 60$ years BP. However, as discussed in section 6.5 these represent minimum ages for the onset of peat accumulation on these profiles, and the dates presented in Avery (1990) suggest that peat accumulation began in the period between $4,010 \pm 120$ years BP and $580 \pm ?$ years BP, which would lend weight to the assumptions made from the pollen analytical evidence presented here.

6.9.4 Conclusions

It was hoped that the search for tephra in sediments from N. Wales would allow its known extent in the UK to be further extended. However, the data presented here seem to raise more questions than they answer. If it is assumed that the diatom/sponge spicule bloom represents a tephra fall, then this pushes the southern limit of Icelandic tephra into N. Wales, although the absence of this layer on Hiraethog, and the small particle size inferred from its complete decomposition would suggest that fallout was sporadic and may possibly not have occurred much further south, at least in detectable quantities. However, questions are raised concerning the fate of tephra in such depositional environments, the dissolution of silicates being a complex and variable phenomenon, and the possible relationship between tephra and bioliths in organic-rich sediments clearly remains a challenge.

The potential of diatoms to provide much information concerning Holocene environmental change was restricted in this study by the sedimentation regime in Llyn y Foel-frech, which could only be ascertained after a palynological study had been undertaken. A clear sequence would have been of great value here in linking vegetation and diatom flora changes, allowing a greater understanding of the environmental changes that have occurred over the Holocene. If another suitable lake can be located in the area and cores recovered from it this may still be possible. A study of phytoliths from Cefn Mawr and the surface soil horizons may also be of further use if adequate identifications can be made, and linked to changes in the vegetation, although this would require the differentiation of grass species in the pollen record wherever possible.

In comparison with tephra and biolith evidence, however, that of pollen from Cefn Mawr provides much useful information concerning the vegetation changes that have occurred over the last $6,175 \pm 50$ years. Until $4,475 \pm 50$ years BP the area was dominated by woodland, which for a period appears to have been unstable. This instability was in a form of reduced tree and increased shrub cover and was possibly due to wetter phases. On the other hand, some evidence points to human interference, and although it is difficult to separate the two, the coincidental peaks in charcoal concentration indicate that these changes were brought about by fire. The absence of charcoal during CM1c suggests that such fires were caused by human activity across the landscape.

The distinct change at $3,530 \pm 55$ years BP also seems to relate to human impact since there is a sudden fall and then stabilising of total tree pollen, suggesting a coppicing regime until $2,805 \pm 50$ years BP when further phases of tree loss occurred, all phases of deforestation having associated evidence of fire in the vicinity. The suddenness of the transition suggests extensive use of woodlands, and this would mean either a rapid influx of people into the area, a possibility not archaeologically evident, or the sudden need of wood for industrial activity, such as mining in the region. However, establishing this link conclusively is not possible from the data available.

Tree depletion initially led to the development of a grassland community, but this gave way to heather at around 2,060 years BP. This further rapid change was possibly climatically induced, being at the boundary between the Sub-Boreal and Sub-Atlantic, but also involved an increase in anthropogenic indicator species, which may represent a greater reliance on arable crops rather than pastoralism, this being the start of the Iron Age when ploughing became more widespread. It is possible that the start of the industrial revolution is also detectable towards the top of the pollen sequence.

Evidence for these changes is vital to an understanding of soil development on Hiraethog over the Holocene. It is obvious that climate and man can have similarly major effects on the vegetation, and this will in turn affect soil development. The increase in *Calluna* led to a build up of organic matter and peat at the surface of some of the soils of Hiraethog, and this will obviously have induced increased waterlogging. This may in turn have caused the formation of ironpans, especially since little tree pollen was found resting on the ironpan suggesting that its development came after the loss of tree cover, a point which is backed up by the AMS dating of these ironpans as discussed in section 6.5. The pollen evidence, however, does confirm the inadequacy of mineral soils in terms of palynological investigations and the lack of movement of pollen into a mineral soil without the influence of soil mesofauna.

Chapter 7. General conclusions and further work

7.1 Introduction

This research project was undertaken with the aim of reconstructing the environmental and pedogenic changes and developments that have occurred in a selected area of the Hiraethog Moors during the Holocene. This required a multidisciplinary approach whereby several techniques were employed to study one problem, rather than one technique being applied to several problems. This included the use of analytical techniques in clay mineralogy, soil micromorphology and palynology. The conclusions drawn here relate to specific profiles and sites but should also be applicable to other upland regions of the U.K. with a shale parentage, since the soils in question are found quite extensively throughout the north and west of the British Isles.

The Hiraethog Moors is an upland area in North Wales dominated by brown podzolic soils (Manod series), ironpan stagnopodzols (Hiraethog series), stagnogleys (Freni series, formally the Ynys series) and peaty soils (Caron series), and it is the history of these that has formed the central theme for this research. Hiraethog is of additional interest in that there is evidence of human occupation of the moorland in the Mesolithic and the Bronze Age, and it is probable that this had an impact on the pedological and environmental development of the area.

There are five main factors which are thought to influence soil development - parent material, climate, vegetation, relief and time (Jenny, 1941). Soil development across North Wales would have begun at the end of the last glacial episode, and so soil age will be constant across much of the landscape. The parent material is relatively similar for all the soil types studied, being periglacial deposits derived from local rock sources, and therefore dominantly of Silurian silt- and mudstones. The soil profiles all lie at very similar altitudes, and thus the climatic conditions influencing each profile at any given point in time are likely to have been similar. Exposure to wave action around the shore of the Aled Isaf reservoir since the 1930's has exposed 3.25km of soil profile, allowing soil sampling and description and providing access to a greater extent of soil profile than could normally be studied at an undisturbed site. It is for these reasons that Hiraethog affords an ideal opportunity to study the relationship between soil development and vegetation. With this in mind an attempt was made to

elucidate pedogenic and vegetation changes for Hiraethog and to link these two aspects wherever possible.

Such soils, in particular the Hiraethog series, have been quite extensively studied in terms of their physical and chemical properties and their clay mineralogy, and so similar analyses were initially carried out to classify the profiles being studied, so allowing comparisons with published data to be made. Three soil types, brown podzolic soil, ironpan stagnopodzol and humic stagnogley were studied and the results confirmed the classifications made by Ball (1960) and Avery (1990). These techniques also allowed some inferences to be made concerning the pedogenic processes which are occurring at the present day and which may have occurred in the past.

Micromorphological investigations were also carried out on these soils to look in more detail for evidence of present and past pedogenic processes. The brown podzolic soil and ironpan stagnopodzol are thought to be members of an evolutionary sequence (Avery, 1990; Bell and Walker, 1992) and so comparisons of the two profiles were carried out in the hope of highlighting differences and identifying the processes occurring in such a sequence.

The environmental conditions throughout the Holocene were elucidated by palynological investigations of sediment cores. This not only allowed vegetation changes to be noted, but also allowed them to be placed in a temporal sequence by means of ^{14}C dating. This facilitated the linking of such changes with known archaeological facts about the site, and upland Clwyd in general, and also with soil development since important features within the ironpan stagnopodzol soil profile were dated by AMS radiocarbon dating.

In the initial phases of this research project other techniques were tried to assess the amount of data they could possibly supply and how feasible it was to carry out such investigations. These included analysis of tephra, bioliths and plant macrofossils. A search for tephra was undertaken with the aim of extending the known southern limit across the U.K. for Icelandic tephra and of using such deposits as marker horizons to allow the correlation of sites in North Wales. However, in the samples studied no tephra was located, and whilst it is realised that the surface area actually sampled may have meant that tephra falls could have been missed, the study did raise some interesting questions concerning the fate of fine-grained tephra falling on such deposits, as outlined in section 6.5. Opaline silica (diatoms, sponge spicules and

phytoliths) and plant macrofossils can provide additional and complementary data to a palynological investigation but due to time constraints it was not possible to carry out extensive studies of these fossils and so they have not formed a large part of this research.

However, the data presented do answer some of the questions which were set out at the beginning of this project. They provide a general overview of the vegetation changes that have occurred across this upland region over the last 6,000 years of the Holocene, changes which have been radiocarbon dated and which are therefore correlatable with those at other sites. They provide a detailed analysis of the present-day characteristics of the three soil types from Hiraethog in terms of their physical and chemical characteristics, their clay mineralogy and their micromorphology. It has been possible to use these pedological data to describe a sequence of events that has occurred during the Holocene, and to answer some of the questions previously raised in the literature.

7.2 Holocene environmental and pedogenic history of the Hiraethog Moors

The following is a reconstruction of the environmental and pedogenic history of the Hiraethog Moors which has been pieced together from the data accumulated for this research project. One point to make in relation to any wider interpretations or usage of these conclusions is that the palynological evidence relates to a wide area, possibly including much of upland Clwyd, whilst the pedological changes described relate to specific profiles, and although the general sequence of events may have been the same elsewhere, the exact timing and duration of these will have depended on the local site conditions for any given profile. The Holocene has been divided into 7 periods based on the main vegetation changes that have occurred which were dated by ^{14}C methods. The descriptions of vegetation changes earlier than 6,175 years BP have come from the literature since data for this period are not available from the sites studied.

>10,000 years BP

It has been suggested (Derbyshire, 1993) that many of the main landscape features of Hiraethog were formed prior to the last glacial episode, although no information is available on the formative agents for these features. It is thought (Livingston, 1991) that such features were modified during the Late Devensian Glaciation when, until around 14,500 years BP, Hiraethog was probably covered by Welsh ice. Livingston

(1991) proposed that, in the final stages of the Late Devensian Glaciation, this would have been in the form of an ice cap centred on Hiraethog with no incursion by foreign ice. This has important implications for soil development since this will have determined the parent materials across the region. Heavy mineral studies have confirmed that the parent material for the soils studied is locally derived Silurian silt- and mudstones. With the loss of ice cover, periglacial conditions influenced this region with the result that solifluction moved glacially eroded materials downslope, re-orienting stone long axes in the direction of the slope, and this has been detected from fabric analyses of these materials. Deposition of minor amounts of aeolian material also occurred at this time. However, the resultant parent material is of local origin, and is similar for all the profiles studied.

The stones within the material in which the brown podzolic soil has formed are oriented in one direction, that of the slope aspect. However, the stones in the material within which the stagnopodzolic soil is developed show two distinct orientations. Both are in the general direction of the slope so the material is still consistent with a periglacial "head" It is possible that, since the underlying solid geological surface is undulating, the two directions of movement represent a divergence of the solifluction lobe around a slight rise in the underlying solid surface. Periglacial conditions also resulted in other features; stone fragments were cracked and clay and silt translocation resulted in the formation of banded cutans. Cryoturbation features, such as stone festoons, can also be seen in some of the exposures around the margins of Aled Isaf.

From the data presented it is obvious that the various profiles which have developed in this parent material differ quite considerably, and this must be due to differences in relief and vegetation since parent material, climate and time are all constants. It is important to note here that although the parent material is all Silurian silt- and mudstones, Warren *et al.* (1984) described this as being frequently banded with alternating layers of mud- and siltstone, and as such the particle size distribution of a soil will be initially determined by the exact sequence of layering and later mixing that existed in the parent material. However, this study would suggest that initially all the profiles were fairly similar indicating that their parent materials must also have been relatively similar.

There is no direct evidence from Hiraethog concerning the vegetation changes that have occurred in the region over this time period, or of any human activity. Earlier Palaeolithic human activity has been inferred from archaeological evidence from

Pontnewydd Cave in the Vale of Clwyd (Green, 1991). However, there is no archaeological evidence to suggest human activity on Hiraethog until the Postglacial. During this period ^{14}C dating of charcoal in the BC horizon of the stagnopodzol indicates that the land surface in these sites was in the order of 1m lower than at the present-day, and therefore the soil profiles would have been shallower and stonier and much more freely drained. Redistribution of clay and silt materials in these soils occurred during this phase and would have been occasioned by a relatively sparse vegetation cover combined with periglacial freeze/thaw processes.

10,000 - 6,000 years BP

During the initial phase of the environmental history of Hiraethog Bell and Walker (1992) suggested that tundra vegetation prevailed, but that with rising temperatures this would have given way to species-rich grassland, scrub and open woodland, which in turn was replaced by closed temperate deciduous woodland during the climatic optimum. By this stage of the Holocene, soils were probably typically brown earths and initially of high base status (Bell and Walker, 1992). Particle size analysis of the lowest and least altered horizons of these profiles shows that the podzolic soils are fairly coarse-textured, whilst the gley has a significantly higher clay and silt content. This may reflect the heterogeneity of the parent material, although it is more likely that the waterlogged nature of the stagnogley profile has resulted in a more rapid disaggregation of stone fragments, and the lack of structural stabilisers, such as Fe^{3+} or organic matter incorporated into the soil, has meant that little structural stabilisation can occur resulting in an impermeable, massive soil. The presence of peds in the stagnogley with brown interiors and gleyed margins indicates the past aerated nature of this soil, again suggesting that gleying caused disaggregation which has led to the textural differences noted.

In the podzolic soils, the presence of ferric hydrous oxides in significant quantities has allowed the formation of structural units which are thought to be fairly stable - removal of iron prior to particle size analysis results in a textural distribution similar to that of the gleyed soil. This highlights a problem with such soils in that, since their prime particles are dominantly silt and clay sized, any breakdown of structure is likely to lead to the development of gleyed properties.

Thus it is possible that, even with high clay and silt contents, these soils were adequately drained brown earth-types during this period. Although chemical and physical analyses can give no further clues regarding this, clay mineralogical

investigations indicate that initially these soils would have been much less intensely weathered. From the pollen analytical results, by the period of the climatic optimum ($\approx 6,000$ years BP) the landscape was supporting a mixed woodland of *Alnus*, *Betula*, *Ulmus* and *Quercus*, which would indicate that the soils were of a higher base status than at present. Micromorphological investigations provide further evidence in support of this. Podzolic profiles show clay deposition in their BC and B_{s2} horizons, and it is suggested (Catt, 1989) that this is a relict feature of the early Holocene when soils were less acidic. Such features are noted in both the brown podzolic soil and the ironpan stagnopodzol, which would indicate that they both have a common ancestor.

The presence of charcoal in the lowest horizon, previously dated to $5,810 \pm 150$ years BP and now to $7,365 \pm 65$ years BP (the latter of *Alnus*) indicates the presence of trees during this stage at these sites. Since these fragments are now between 50-100cm beneath the mineral soil surface it suggests that a/several phase(s) of erosion occurred around this time to bury these fragments, although it is possible (but unlikely) that they represent roots burnt *in situ* beneath the surface of the soil; if this was the case then it should be possible to pick up the presence of maghemite in the soil matrix surrounding the fragments. It is likely that soil mixing by faunal activity was a feature of these soils at this time, but since the charcoal fragments are located in the lowest, and stoniest, horizon it is possible that after burial of these materials faunal activity in this horizon would have been minimal. The fragments located therefore probably represent the level of the former land-surface.

However, their concentration at this point along with flint fragments rather than distributed extensively throughout the soil suggests erosive phase(s) may be the correct explanation especially since the location of these profiles in the lower slope facets would make them ideal sites for the accumulation of colluvium. This would have meant that the soils, during this period, would have been shallower and stonier and so naturally more freely drained. These dates also indicate that the cutans, noted in the BC but not in the overlying mineral horizons, must be older than $7,365 \pm 65$ years BP. This suggests that they were formed during periglacial conditions, although the banding with coarser material may represent phases of vegetation disturbance occasioned by human activity. Conclusions concerning the role of vegetation disturbance in this are not possible at present since the pollen stratigraphy does not extend beyond $6,175 \pm 50$ years BP at this site.

Brown earths can be found in pockets across Hiraethog, and indeed some even carry populations of moles. This indicates that earthworms are present now, and since it is

probable that such areas were more widespread in the past, so would have been the activity of the soil fauna. One feature commonly cited as evidence for the previous brown earth nature of these soils is the spongy B_s fabric (Sanborn and Lavkulich, 1989b). This again is found in both the podzolic soil types indicating that similar processes have operated, or are operating now, in them. It is often suggested that this fabric was produced by earthworm activity in the soil and that it has been preserved as such even though the soils are now too acidic for earthworm activity. However, as outlined in section 6.4.2, there are several reasons to doubt this explanation. It is possible that earthworms have been active in these soils in the past, but it is more likely that any features produced during this pedogenic phase have since been lost from the soil. The presence of earthworms in similar soils has been inferred from micromorphological evidence in other areas (Maltby and Caseldine, 1982), but this has all come from soils buried beneath archaeological monuments and so isolated from further pedogenesis. The spongy fabric noted in the B_s horizon of these soils is not thought to be a relic feature of past earthworm activity but due possibly to more recent physical and chemical processes.

6,000 - 4,500 years BP

This is the period where evidence for vegetation changes comes directly from the Hiraethog Moors, as outlined in section 6.9. It is a period when woodland cover remained stable and there was little herbaceous vegetation although woodland species were fluctuating and were being replaced by shrubs. This may simply reflect natural processes, although this is the period when archaeological and charcoal evidence points to an occupation of the moorland at least at Aled Isaf and Brenig, and possibly at other as yet unidentified sites. This coincides with the Mesolithic, again indicating a human cause for the vegetation fluctuations noted, especially since such fluctuations were not identified during the following period.

One factor which is thought to be of importance in the podzolisation process is the presence of allophane in the lower horizons of podzols (Farmer, 1984). Significant oxalate extractable quantities of Si and Al would be suggestive of the presence of amorphous materials but, in contrast to other studies, such material could not be detected chemically or micromorphologically in the profiles studied. However, the stagnopodzol showed evidence of thin pale yellow birefringent argillans, which were not noted in the brown podzolic soil. This must relate to a difference in the processes that have occurred in these two profiles towards the end of the clay translocation phase. In the brown podzolic soil, thin argillans occur, but these are red-brown in

colour which would suggest that either those in the stagnopodzolic soil have been reduced subsequent to deposition or, since no other features show signs of reduction, that this clay material had come from a zone of more intense weathering where iron depletion had already occurred, such as the E_{ag} . This suggests that the stagnopodzolic profile may have undergone more intense weathering and leaching during this earlier period of its development.

Such features must have formed post $7,365 \pm 65$ years BP (or post $5,810 \pm 150$ years BP). These are dates for a possible period of erosion and profile build up at these sites. The features described are found in the material which was deposited at this time and must therefore relate to processes occurring after this period of erosion and deposition. This would confirm the assumption that the formation of the E_{ag} horizon in the stagnopodzol, and possibly the podzolisation processes, did not begin until after around 6-7,000 years BP.

This may have important implications later on in the history of these soils. Peat development seems to have commenced due to a climatic shift at the boundary between the Sub-Boreal and the Sub-Atlantic. However, it did not occur in all soils, and if the present stagnopodzolic soil was more intensely leached early on in its development, resulting in lower pH values and base-status, this may have prompted a shift to more acidophile vegetation communities, along with the climate becoming wetter and cooler, causing peat accumulation on these, but not on other, soil profiles.

The logical explanation for the development of up to 1m of soil profile, with charcoal and flints being buried at depth, during the period 6,000 years BP to 4,000 years BP, is a phase of erosion and downslope movement of soil. This could have occurred in one short-lived event, or by slower soil creep processes. However, soil erosion is indicative of an unstable soil surface, which usually results from a disturbance of the vegetation cover. Since prolonged disturbance does not occur during this time period, but short-lived phases of disturbance do, it may be that during such periods erosion occurred. This would account for the buried charcoal and flints noted in the lower horizons of these profiles and the fact that some of the charcoal fragments dated give an older age of $7,365 \pm 65$ years BP. The fine argillans noted in the podzolic profiles may be an indication of this. Erosion would have led to the deposition of soil material on the surface of the soil profiles, and such a process indicates a lack of vegetation cover at the time. This could have resulted in the redistribution of fine-grained soil components down the profile before the vegetation community had re-established itself.

4,500 - 3,500 years BP

The period 4,500 years BP to 3,500 years BP saw a more stable woodland component, probably *Quercus/Ulmus* woodland in the valleys and more open *Betula/Alnus* woodland across the upland region. During this time natural soil acidification will have been taking place, and it has been suggested (Bell and Walker, 1992) that incipient podzolisation was also occurring in these soil by this time with the development of an $E_{a(g)}$ horizon at some sites. Certainly, the development of the E_{ag} horizon probably did not begin until after 6,000 years BP. This would depend on there being adequate drainage and it is possible that, in the poorly drained sites occupied today by the stagnogley, this was not the case, and that these soils remained as brown earths, probably with some level of gleying due to the low relief.

3,500 - 2,800 years BP

The main change in the vegetation community occurred at 3,500 years BP with a sudden decline in woodland cover to be replaced initially by a grassland vegetation community and then by heathland vegetation types. From the suddenness of this change and the coincident peaks in charcoal concentration, it was almost certainly caused by human activity, although it is difficult to be certain about the form that this took. The sudden loss of tree cover followed by a period of stability is suggestive of a coppicing regime, with the trees flowering potential reduced. It is possible that the amounts of wood needed to supply the Bronze Age metal workings on the coast would have required a coppicing system, but it is unlikely that this would have come from an area such as Hiraethog, the distance being too far. However, clearance did take place on Hiraethog at this time, at least in the vicinity of Cefn Mawr. Since it is possible that the upland woodlands may have been fairly open it is also possible that the pollen diagram presented here represents both local and regional changes, and may therefore depict a coppicing regime some distance from Hiraethog. It is a time when anthropogenic indicator species, such as *Rumex*, become more abundant. This is indicative of the fact that pastoralism and/or arable farming was probably taking place, or at least taking place at a level now detectable in the pollen diagram. This would correlate with the palynological evidence obtained by Hibbert (1993) for the Brenig Valley, where it has been suggested that, during the Late Neolithic, parts of the moor were already in use for sheep and cattle grazing.

This vegetation change, and the further passage of time, will have resulted in changes occurring in the soil profiles. Natural soil acidification and a cessation of soil faunal activity as pH values became too low will have been taking place, but a loss of the tree canopy will have increased water movement through profiles and intensified the leaching and degradation of the soils. In the more poorly-drained sites this probably led to increased wetness, a gradual reduction in iron and its subsequent loss from the profile. With no further incorporation of organic matter into the mineral soil, organic carbon levels would have fallen and peds would have become increasingly unstable resulting eventually in enhanced water retention and gleying. From pollen analysis, peat accumulation began in such sites when tree pollen values were fairly low, indicating that this happened after the major phase of deforestation had taken place. Without more detailed radiocarbon dating it is, however, difficult to place peat initiation, in relation to vegetation stages, at such sites more precisely.

Clay mineralogical studies show that by 6,000 years BP vermiculite had begun to form from the breakdown of hydrous mica along with a gradual loss of chlorite from the most weathered horizons. In waterlogged sites this alteration would have continued and would have been further facilitated by the loss of protective iron and aluminium coatings. However, the waterlogging in these profiles and the subsequent reduced water movement down through the profiles has meant that chlorite has not been weathered out of the surface mineral horizon, and the continued build up of peat at the surface may have served to isolate the mineral soil completely from the weathering environment. From this it may be reasonable to suggest that waterlogging in these sites occurred soon after the loss of tree cover and the exposure of the soils to increased leaching, since prolonged weathering would have caused a greater reduction in the quantity of chlorite present in the uppermost horizon. It may be, therefore, that once these soils became permanently waterlogged pedogenic activity became very slow, resulting in little further change in profile characteristics.

With this loss of the protective tree canopy and the resultant increase in leaching intensity, it is probable that podzolisation processes began, or intensified, on the better drained sites. From the data presented here it is difficult to determine which of the current theories of podzolisation is most applicable to the soils of Hiraethog, but it is likely that the present-day brown podzolic soil and the ironpan stagnopodzol profiles were very similar at this stage although the development of a mor humus layer at the surface of the stagnopodzolic profile had possibly already begun.

2,800 - 2,060 years BP

This phase of landscape evolution of the Hiraethog Moors saw woodland continuing to decline, being replaced by Gramineae, with the first appearance of *Plantago*, indicative of increased agricultural activity in the landscape. Fluctuating tree pollen values, dominantly of *Betula*, suggest that woodland clearance was still occurring, followed in some cases by abandonment allowing re-invasion by tree species. During this time podzolisation and soil acidification processes continued, and that in poorly drained sites the continued removal of iron from profiles resulted in further structural collapse and increased waterlogging. At the surface of the stagnopodzol and stagnogley mor humus would have been accumulating. In the case of the stagnopodzol this is likely to have led to a greater intensity of weathering in the surface mineral horizon, resulting in further loss of chlorite from the horizon.

2,060 - present-day

During the final stage in the environmental history of the Hiraethog Moors, a continued decline in woodland cover was accompanied by an increasing area of *Calluna*, with the climate becoming wetter and colder into the Sub-Atlantic. Peat began to accumulate at the surface of the ironpan stagnopodzol and the stagnogley, but not at the surface of the brown podzolic soil, and it is this which is most likely to have caused the differences in these profiles seen today.

It is likely that both podzolic soils were of a similar character, *ie.* brown podzolic, prior to the build up of peat, but that the presence of peat and the associated surface gleying led to the differences noted. The B_{s2} horizon of both the brown podzolic soil and the stagnopodzol are fairly similar, but the overlying horizons are markedly different, and from analyses it seems as if the stagnopodzolic characteristics could have been superimposed on those of an earlier brown podzolic phase, occasioned by a build up of organic matter and peat at the surface of the soil profile.

In the brown podzolic soil, both the B_{s1} and B_{s2} give similar particle size cumulative curves, whilst in the stagnopodzolic soil the respective curves are quite different, the B_{s1} having a higher clay and silt content. The reason for this becomes clear when the chemical data are analysed which also has implications for the clay mineralogy and the micromorphology. Extractable Fe in the brown podzolic soil (B_{s1} and B_{s2}) and the B_{s2} of the stagnopodzol is concentrated in the clay fraction, whilst in the B_{s1} of the stagnopodzol iron is concentrated in the >2µm<2mm fraction. When iron oxides

are in the clay fraction they are more likely to be capable of binding soil particles together throughout the soil, whilst when in a larger size fraction the distribution is likely to be more sporadic and therefore the influence of iron on the structural stability will not be as great. This change in ferric hydrous oxide distribution resulted in the more massive structure noted for the upper B_s .

Analysis of the ratios of the different extractable iron fractions supplies some information about the processes which are operating in these respective horizons. Fe_d/Fe_p ratios, which can be used to indicate the relative ageing of iron hydrous oxides, are high in the ironpan and the B_{s1} of the stagnopodzol. This suggests that these horizons are relatively stable and are not at present being added too. However, the B_{s2} of the stagnopodzol has lower ratios, suggesting this horizon is, at present, more active and is a zone of iron illuviation - the iron probably having come from higher up the profile.

The clay mineralogy of the B_s of the stagnopodzol differs from that of the brown podzolic soil. In the latter clay mineralogy is constant throughout the B_s . In the stagnopodzol the upper B_s seems to be closer to the overlying mineral horizons than to the B_{s2} , in that it contains little chlorite but more vermiculite and lepidocrocite. This is indicative of a greater intensity of weathering in the upper B_s horizon. This investigation seems to suggest a sequence of development from chlorite/hydrous mica \Rightarrow chlorite/hydrous mica/vermiculite \Rightarrow hydrous mica/vermiculite/HIV in the soils of Hiraethog as the intensity of weathering increased. This would seem to confirm the proposal that brown podzolic soils developed into stagnopodzolic soils with the build up of peat at the surface.

Since it has been shown (Wang *et al.*, 1989) that the presence of iron and aluminium hydrous oxides in a soil can protect clay minerals from weathering, the fact that the B_{s1} has iron concentrated in the larger size fractions may explain this clay mineralogical difference since iron will not be available to coat and so protect minerals, leaving them vulnerable to weathering. This is clearly exemplified in the micromorphology of the two horizons; the B_{s2} has a spongy fabric with a general red/brown colour whilst the B_{s1} has a paler colour with iron concentrated in nodules.

Pollen analytical data suggest that peat development across Hiraethog began during a phase when the landscape was not wooded, and grassland was giving way to heathland. This change occurred over Hiraethog at the boundary between the Sub-

Boreal and Sub-Atlantic climatic periods, and is therefore likely to have been initiated by the climatic shift which occurred.

The dates presented in Avery (1990) suggested that peat development began on these stagnopodzolic profiles between 4,000 years BP and 580 years BP, and that ironpan development began around 1,500 years BP. Pollen analytical evidence from the surface O_h horizons indicates that peat development began at the interchange between grass and heather vegetation, some 2,060 years ago which correlates with these data. Analysis of the pollen in the E_{ag} horizon also seems to suggest a similar time period for the existence of this horizon and of the distinctive cracks that run vertically through it.

However, it would seem that the vegetation change to a more acidophile community allowed the accumulation of organic matter at the surface of some brown podzolic soils, initially as mor humus causing an intensification of weathering and a continued loss of chlorite and then as peat leading to gleying in the surface mineral horizon and a redistribution of iron to produce an ironpan. As protective iron and aluminium hydrous oxides were lost, so weathering of chlorite continued leaving very little or no chlorite in this horizon, whilst in profiles not affected by peat this process did not occur. With increasing peat depth, waterlogging began to have a deeper influence in these profiles, and is currently causing some redistribution of iron in the B_{g1} , with subsequent effects on the clay mineralogy and micromorphology.

The final difference between the podzolic profiles is the presence of the ironpan (B_f) in the stagnopodzolic soil profile. The ^{14}C date published in Avery (1990) suggests that this feature is at least 1,400 years old and therefore its presence may have led to the waterlogging of the upper mineral horizon and subsequent peat accumulation. Subsequent dating of the ironpan confirms the date presented in Avery (1990), and again suggests that peat accumulation followed ironpan development. However, interpretations of analyses and dating of the fractions of organic C held in the pan is not conclusive, and because of the nature of the mineral soil materials being dated and the relatively shallow nature of the surface peaty accumulation the possibility of errors and/or contamination is such that no definite conclusions can be drawn. The consistency of the dates presented in Avery (1990) and this thesis suggests, however, that such uncertainties may be resolved by more extensive analysis and dating of the organic C fractions.

Evidence presented here and in the literature points to peat accumulation leading to ironpan development by inducing waterlogging in the surface mineral horizon. Often in gleyed soils iron precipitation is associated with manganese precipitation in distinct bands or zones depending on the exact redox characteristics of the soil. In these profiles there is no such differentiation in the ironpan, and this would indicate that these soils are not at a suitable Eh/pH regime to result in a differentiation of Fe and Mn, although Bower (1970) suggested that there was some concentration of Mn in the Hiraethog series ironpan as a trace element.

The fact that the clay mineralogy of the pan indicates that the ironpan is formed in material deficient in chlorite suggests that ironpan formation followed surface waterlogging, iron loss and chlorite weathering. This would not necessarily require the complete loss of iron from the horizon as exemplified by the Bs1 which has iron concentrated in the larger size fractions resulting in a loss of chlorite from the profile. Thus in this final phase of pedogenesis the brown podzolic soil was transformed into an ironpan stagnopodzol by the accumulation of peat at the surface of the profile.

Present-day land use includes coniferous plantations, water management and upland sheep grazing. Sheep grazing, and the previous management of Hiraethog as a grouse moorland by burning, will perpetuate the heathland vegetation community and so allow a continuation of the leaching and weathering processes occurring in these soils. The practice of peat cutting, which has taken place on Hiraethog in the past, is also likely to have influenced the mineral soils, especially gleyed soils which may have previously been isolated to some extent from the weathering environment. Weathering of clay minerals in these profiles may now be occurring again, or at least occurring at a faster rate.

7.3 Conclusions and summary table

This research project set out to answer a number of questions concerning the environmental and pedogenic history of the Hireathog Moors, using a multidisciplinary approach, and although the results presented here resolve some of the previously outstanding problems, there is still much scope for further work to be carried out on this subject. The results presented in this thesis allow soil profiles exposed around the margins of the Aled Isaf reservoir to be characterised according to the S.S.E.W scheme, and for present-day pedogenic processes to be assessed. Vegetation change over the last 6,000 years has been elucidated and placed in an absolute time framework. Soil development was studied, and a sequence of events

leading to the formation of the soil profiles present today has been outlined, with some of the events tentatively placed in the time framework by radiocarbon dating.

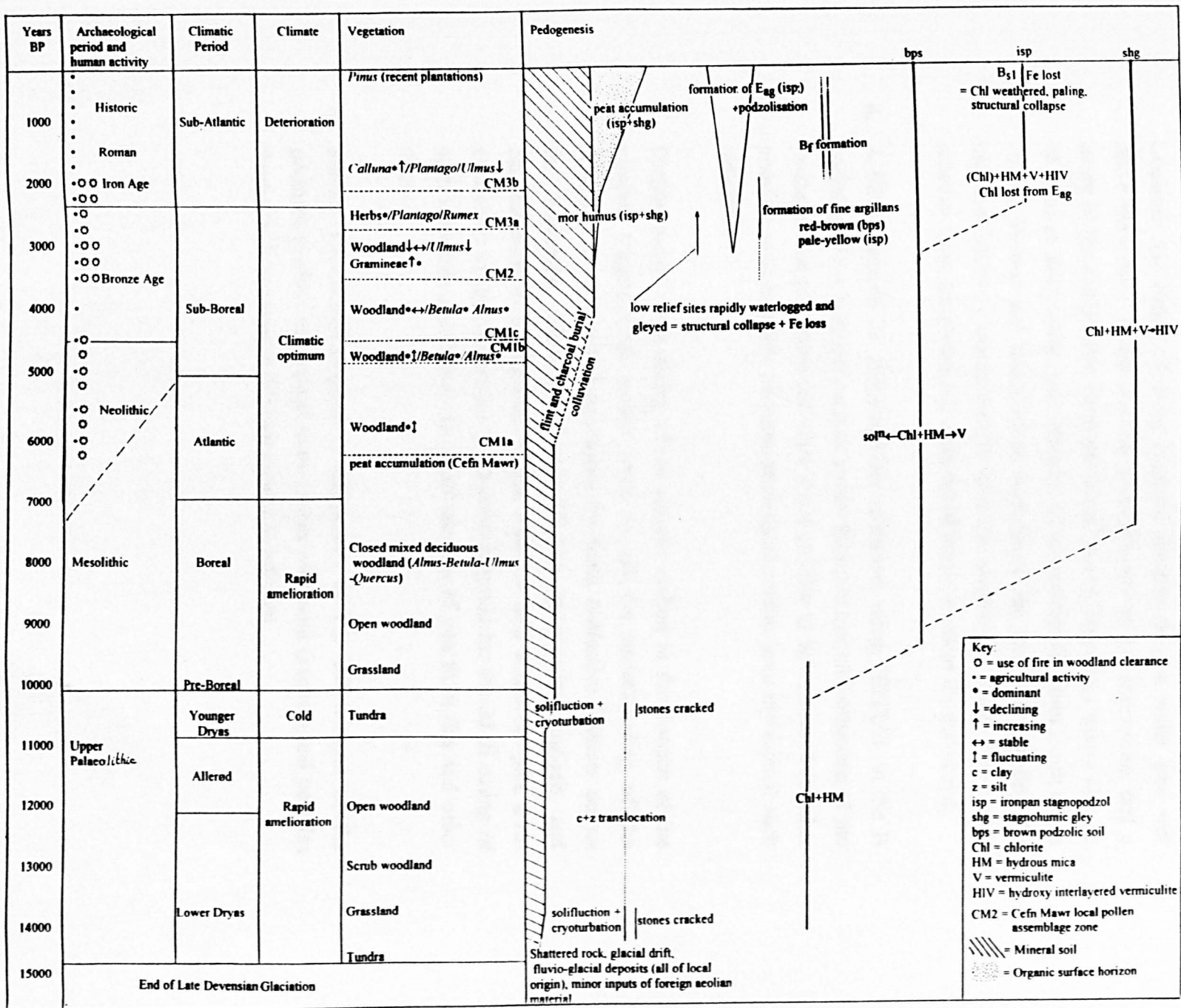
These results extend the knowledge of this upland region and allow the archaeological evidence from Aled Isaf and Brenig to be interpreted in terms of the changes that were occurring in the environment over the Holocene. This information, although specific to the sites studied, does have relevance to other upland regions with a Silurian silt- and mudstone parent material, such as central Wales, parts of the Lake District and the Southern Uplands of Scotland.

7.3 Further work

With the wide range of topics covered by this project there is obviously scope for more work to be carried out to increase the understanding of the processes involved. The following are suggestions which may help solve some of the outstanding problems.

1. The location and study of a natural lake from Hiraethog with a complete sediment record, in terms of pollen, diatoms, macrofossils and tephra, may further the understanding of the pollen sequence described for Hiraethog and possibly allow the distinction to be made between local and regional pollen. Analysis of the diatom flora in relation to this would aid the understanding of the impact of vegetation change on the soils of the catchment.
2. A search for tephra in any sediment cores recovered would help to set the southern limit for Icelandic tephra in the British Isles. The presence of biolith blooms, as noted in this thesis, would provide additional data concerning the fate of such particulate matter being deposited in the lakes and peat bogs of upland regions.

Table 6.13 Summary of the Holocene environmental, pedogenic and archaeological history of the Hiraethog Moors (incorporating information from Table 4.1).



3. Detailed fabric and microfabric analysis of all horizons of the soils exposed around the margins of Aled Isaf may allow the reasons for the presence of flints and charcoal at depth in the profiles to be clarified. Location and dating of other charcoal samples from a wider area will allow the extent of this possible erosion event to be determined, and a study of the soil profiles from the slopes above these sites would also be of value in interpreting such features. If no charcoal fragments with a pith can be located and identified an analysis of the fabric surrounding the charcoal could be undertaken to look for maghemite which may clarify whether these fragments represent wood burnt *in situ* in the soil or not.
4. A further search for allophanic-like materials, using HRTEM, in the B horizons of the podzolic profiles would facilitate our understanding of the podzolisation processes and allow these profiles to be compared to other podzolic soils in which micromorphological studies have highlighted such materials.
5. Further analysis and dating of the organic carbon in the ironpan of the ironpan stagnopodzol would serve to aid the understanding of the formative processes and conditions for these distinctive features across the landscape. This would require the quantitative analysis and determination of the various organic fractions held within the pan, a re-evaluation of the preparation procedures required for the AMS dating of such materials and further dating of samples of pan from this and other sites.
6. Further micromorphological investigations of the BC horizon of the podzolic profiles may reveal more stones with both cracking and pellicles from which a sequence of events could be inferred.

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APPENDICES

Appendix I

Changes in percentage area for selected features with increasing point count totals.

	Total count	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Pedofeatures
Brown	100	20	33	25.0	0.0	0.0	21.0	0.0	1.0
Podzolic	400	12	30.5	20.2	0.2	0.0	36.7	0.0	0.4
BC	600	12.1	28.1	21.3	0.5	0.0	37.9	0.0	0.1
	800	10.3	28.0	21.9	0.4	0.7	38.0	0.0	0.7
	1000	11.2	29.6	23.0	0.3	0.5	34.9	0.0	0.5
	1300	10.9	29.9	23.3	0.3	0.4	34.5	0.0	0.7
	1500	10.8	30.1	23.4	0.4	0.4	34.1	0.0	0.8
	1800	10.8	30.0	23.3	0.4	0.3	34.4	0.0	0.8
	2000	10.9	29.9	23.4	0.3	0.4	34.2	0.0	0.9
	2200	10.8	30.0	23.4	0.4	0.4	34.3	0.0	0.7
Ironpan	100	24.6	0.4	14.2	11.9	0.1	0.7	48.1	0.0
stagnopodzol	300	22.1	0.7	14.9	8.6	0.1	2.4	49.9	1.3
E _{ag}	500	20.4	0.6	15.8	9.4	0.4	2.4	49.2	1.0
	800	19.9	0.5	16.1	8.1	0.4	2.0	51.9	1.1
	1000	19.2	0.7	15.7	7.7	0.5	2.3	53.0	0.9
	1250	19.6	0.6	14.9	7.9	0.6	2.1	53.5	0.8
	1500	19.4	0.7	15.2	8.0	0.5	2.2	53.0	1.0
	1800	19.5	0.6	15.2	7.9	0.4	2.2	53.3	0.9
	2000	19.6	0.7	15.1	7.8	0.4	2.1	53.5	0.8
	2200	19.6	0.7	15.0	7.8	0.5	2.2	53.2	1.0

Appendix II

Physical and Chemical Data for the ironpan stagnopodzol profiles, the brown podzolic profile and the stagnohumic gley profiles.

- a** Fabric analysis of soil parent materials.
- b** Heavy mineralogy of 200-63 μ m fractions.
- c** Summary of particle size distribution curves for ironpan stagnopodzol, brown podzolic and stagnohumic gley profiles.
- d** Cumulative particle size distribution curves for ironpan stagnopodzol, brown podzolic and stagnohumic gley profiles.
- e** Soil colour.
- f** Physical and chemical data (including graphical representation) of a) ironpan stagnopodzol profiles b) brown podzolic profile c) stagnohumic gley profiles.
- g** Extractable amorphous materials in soil clay fraction.

Appendix IIa. Fabric analysis of soil parent material

Podzolised brown earth				Ironpan stagnopodzol			
Angle of dip °	Direction	Long axis cm	Short axis cm	Angle of dip °	Direction	Long axis cm	Short axis cm
28W	215	7.6	5.3	9W	225	12.0	5.6
10E	182	5.7	2.3	21E	229	7.1	5.0
22W	184	3.6	2.0	9E	220	12.9	5.6
12W	180	3.0	2.0	9E	274	13.2	3.6
17E	156	4.2	2.5	4E	269	10.0	4.6
6W	164	9.0	6.5	0	231	10.0	4.4
25W	175	5.5	3.6	4E	229	6.2	4.4
19E	179	5.7	3.5	13E	270	5.5	2.7
16W	149	9.2	4.5	4E	225	14.4	5.4
24E	181	9.2	1.4	15E	300	8.0	3.9
5W	199	6.2	5.0	30E	229	6.9	3.0
16E	179	6.2	2.0	12E	221	7.0	2.2
40W	180	7.1	2.0	7E	224	8.3	3.3
28E	176	6.5	2.0	10E	269	10.2	2.1
6E	151	3.5	1.4	5E	274	10.5	4.4
2W	182	6.7	3.0	5E	273	7.9	5.4
16W	181	3.8	1.5	9E	277	12.5	7.6
16W	164	2.6	2.3	9W	271	6.0	3.6
8W	185	4.5	1.3	2W	234	6.5	2.7
16W	171	4.7	2.3	16E	264	6.3	3.3
18E	211	3.6	1.0	2W	226	10.0	4.5
32E	209	6.3	5.0	0	227	5.9	4.7
6E	221	3.1	3.0	19W	230	8.4	3.9
16W	219	4.1	2.2	2W	233	10.0	7.0
34W	142	4.0	3.2	11E	223	9.5	3.8
14W	178	2.5	1.2	18W	270	14.5	5.0
34E	210	4.0	2.5	19E	244	8.0	4.4
14E	215	4.2	1.5	28E	234	6.2	3.0
31W	159	5.1	2.4	24E	274	11.5	5.0
18E	183	3.2	2.4	8W	263	8.9	5.8
40E	176	4.0	2.6	32E	226	6.2	4.9
10W	165	3.6	1.7	8W	225	8.6	2.6
10W	171	5.6	3.1	28E	223	9.8	4.9
2E	161	8.8	6.1	68E	274	6.5	2.0
2W	153	4.9	2.1	24W	277	8.4	2.7
22W	220	2.2	1.5	40E	233	5.0	1.8
4E	184	5.0	2.6	30W	295	4.0	3.2
16W	187	4.2	2.3	14E	225	6.3	2.6
8W	172	5.0	2.5	14E	225	4.0	2.5
47E	181	4.5	5.7	6E	274	4.0	1.8
8E	189	10.5	2.7	30E	247	4.4	1.5
17W	174	5.0	1.7	38E	299	8.9	3.9
4W	176	2.5	4.5	32E	263	3.0	1.5
2W	184	9.0	3.5	40E	269	5.0	2.0
8W	191	3.7	4.3	30E	241	3.6	1.2
4E	210	5.6	2.7	8W	271	7.3	1.9
8W	149	4.5	2.7	12W	270	10.0	3.0
10E	183	6.2	4.2	20E	276	5.3	1.7
11W	177	7.3	3.7	38E	224	5.4	1.4
2W	180	4.1	2.1	16E	271	6.1	2.6
		n=50 r=5.22 SD=1.99	n=50 r=2.86 SD=1.33			n=50 r=7.92 SD=2.86	n=50 r=3.59 SD=1.51

Appendix IIb. Heavy mineralogy of 200-63 μ m fraction.

Ironpan stagnopodzol.

Profile 1		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Eag	0.12	6	2	3	2	1	1	-	-	-
Bs1	0.12	7	2	2	1	1	1	-	-	-
Bs2	0.15	7	3	2	1	1	-	-	-	-
BC	0.31	8	3	2	1	-	1	-	1	-

Profile 2		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Eag	0.15	6	3	2	1	1	1	-	-	-
Bs1	0.11	7	3	3	1	1	1	-	-	-
Bs2	0.19	8	3	3	2	1	1	1	-	1
BC	0.36	8	3	3	1	1	1	-	1	-

Profile 3		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Eag	0.11	6	3	2	2	1	1	-	1	-
Bs1	0.14	7	2	2	2	-	1	1	1	-
Bs2	0.18	7	2	2	1	1	-	-	-	-
BC	0.31	8	3	3	1	-	-	-	1	-

Typical brown podzolic soil

Profile 1		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Ah	0.18	7	2	2	2	1	1	-	1	-
Bs1	0.19	7	3	2	1	-	1	-	-	-
Bs2	0.22	7	3	2	1	-	1	-	-	1
BC	0.42	8	3	2	1	-	1	-	1	-

Cambic stagnohumic gley

Profile 1		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Eag	1.14	7	3	2	1	-	1	1	-	-
Bg	1.51	7	3	2	1	-	1	-	-	1
BCg	0.50	8	3	3	2	-	1	-	-	-

Profile 2		Chl.	Tourm.	Zirc.	Rut.	Brook.	Clinoz.	Amphib.	Epid.	Kyan.
	%									
Eag	0.56	7	3	2	1	-	1	-	1	-
Bg	0.63	7	2	2	1	-	1	1	-	-
BCg	0.95	8	3	3	1	1	1	-	1	1

Key:

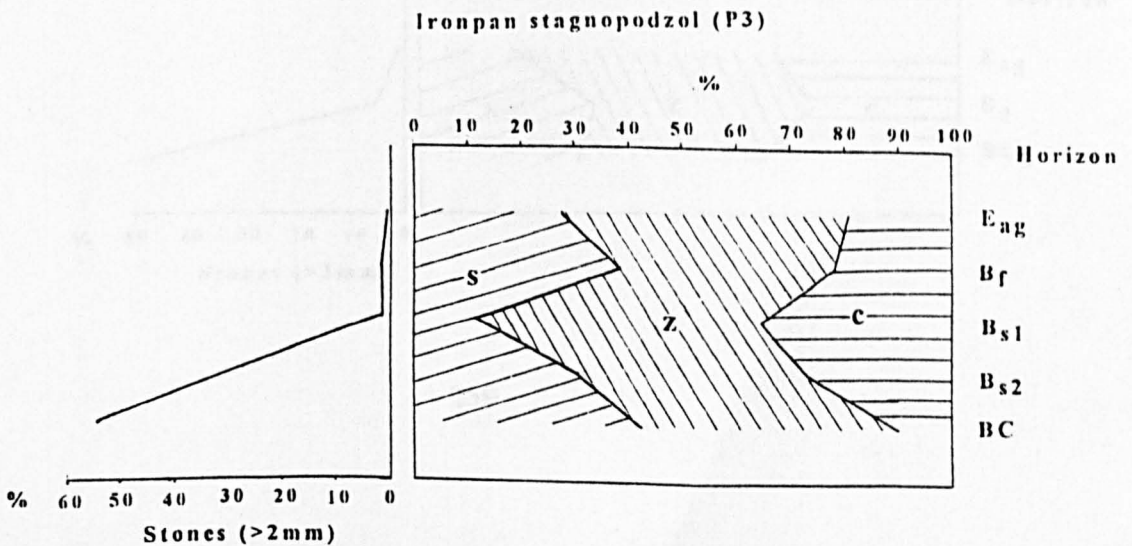
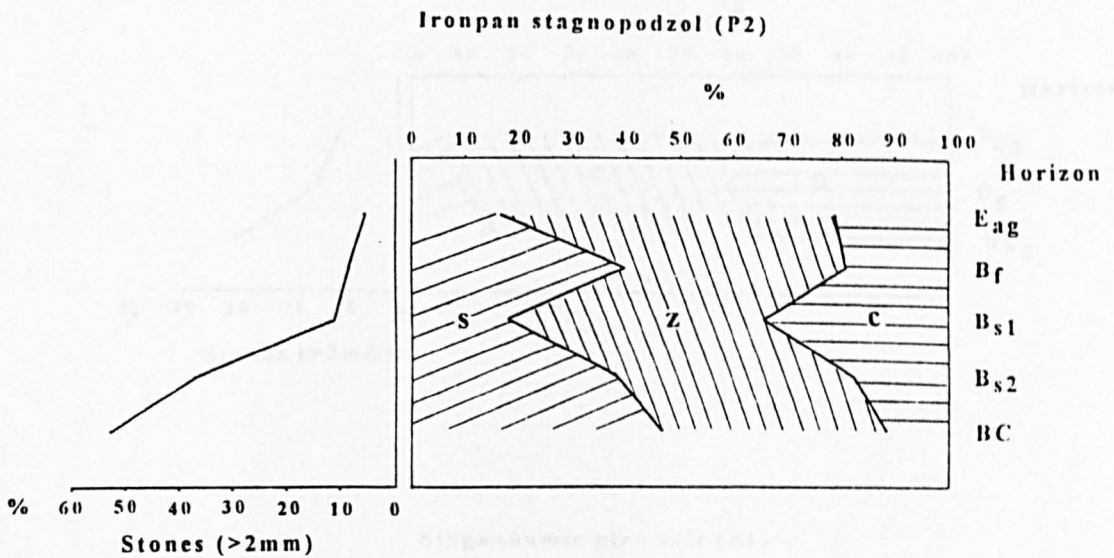
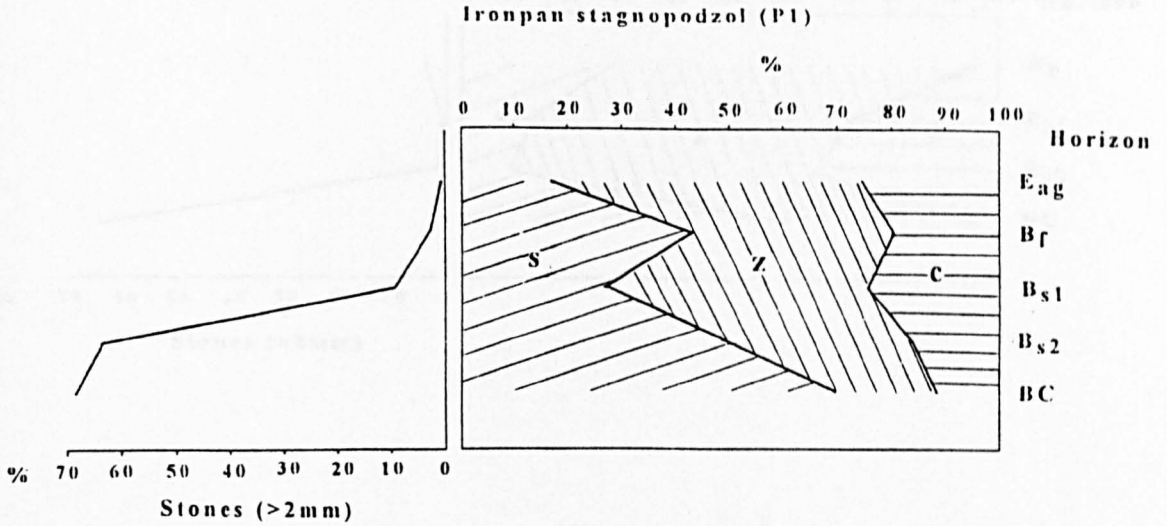
Chl. = chlorite
Tourm. = tourmaline
Zirc. = zircon
Rut. = rutile
Brook. = brookite
Clinoz. = clinozoisite
Amphib. = amphibole
Epid. = epidote
Kyan. = kyanite

Scale: (Jenkins, pers. comm., 1991)

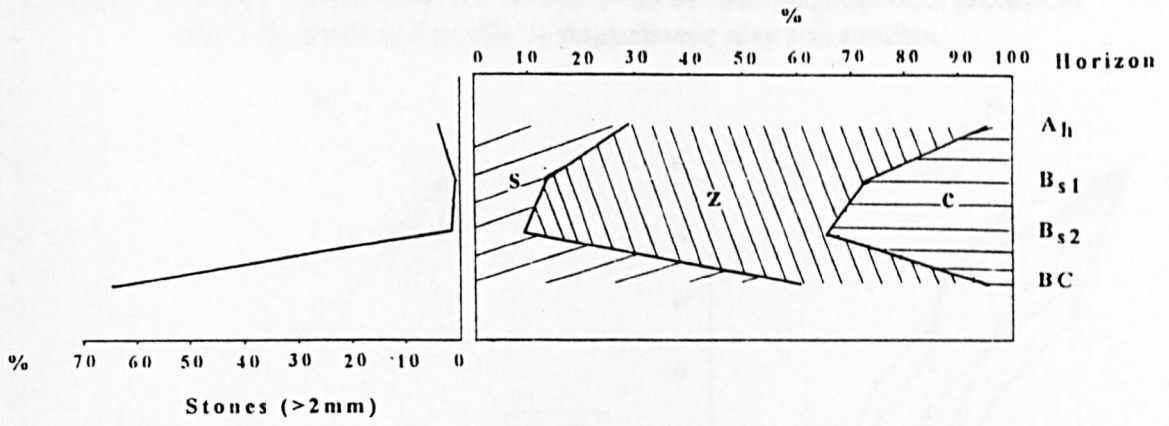
8 - monomineralic
7
6 - abundant
5
4 - common
3
2 - occasional
1 - trace
-- absent

Appendix IIc

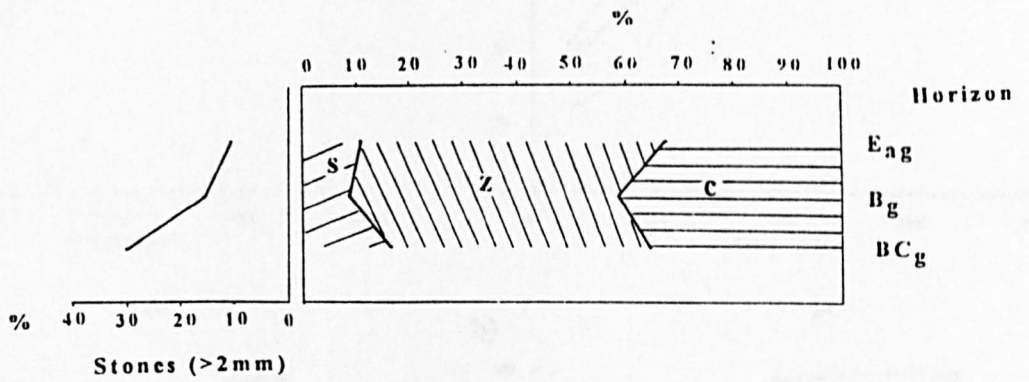
Summary of particle size distribution for ironpan stagnopodzol, brown podzolic and stagnohumic gley soil profiles.



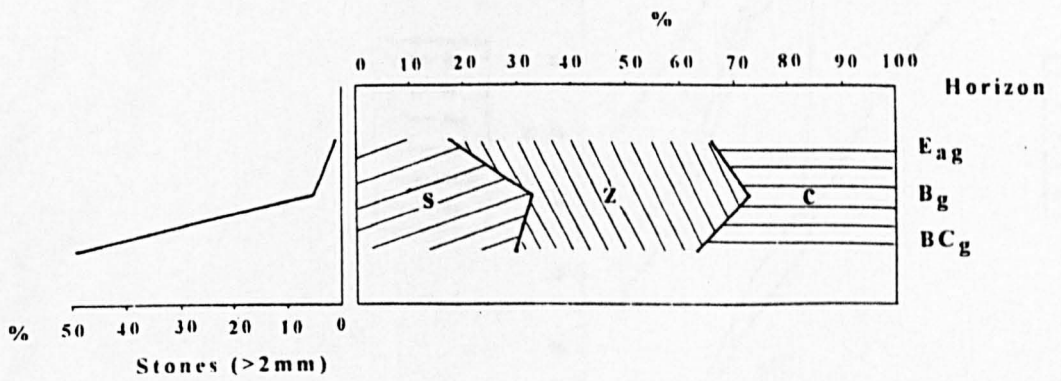
Brown podzolic soil



Stagnohumic gley soil (P2)

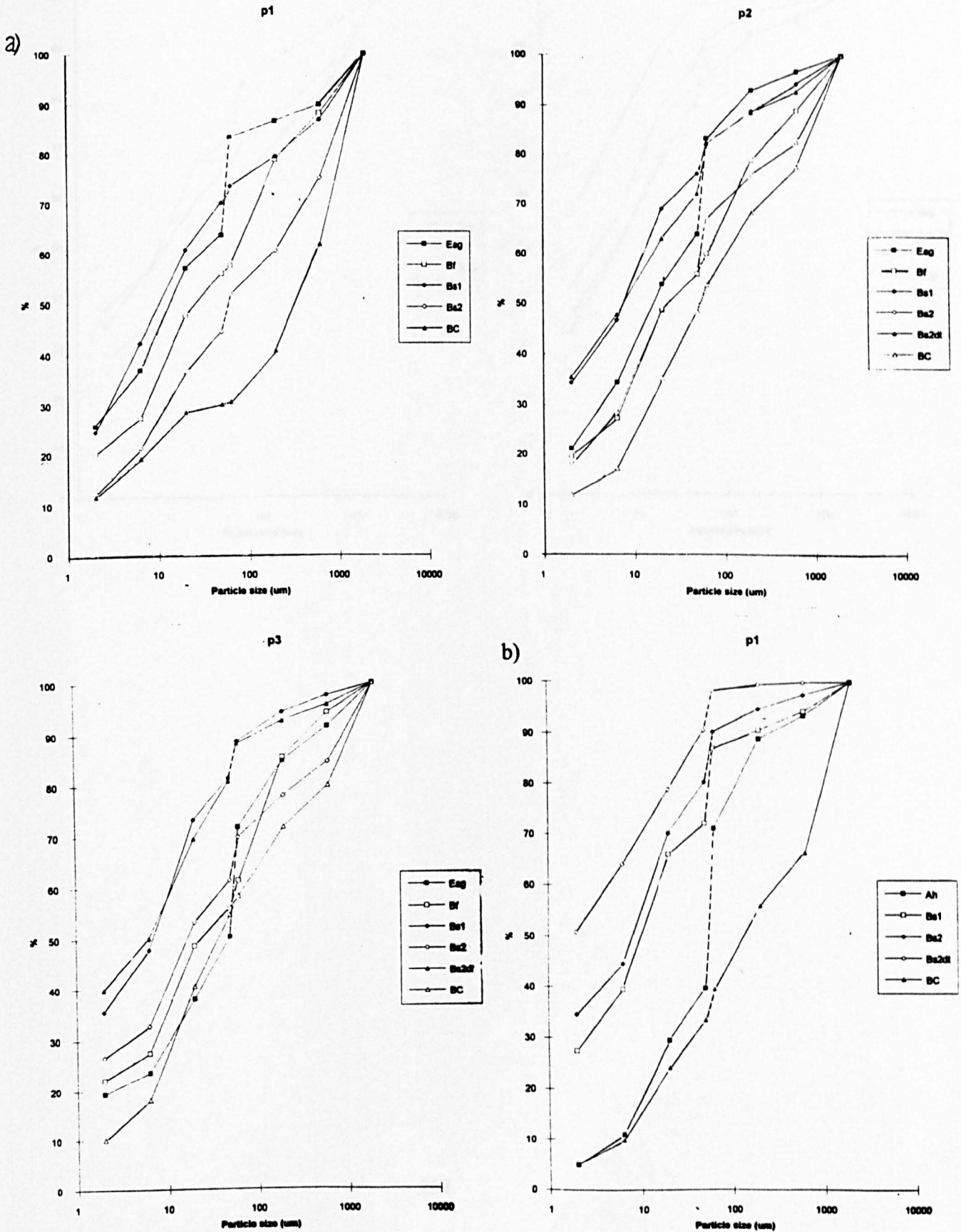


Stagnohumic gley soil (P1)



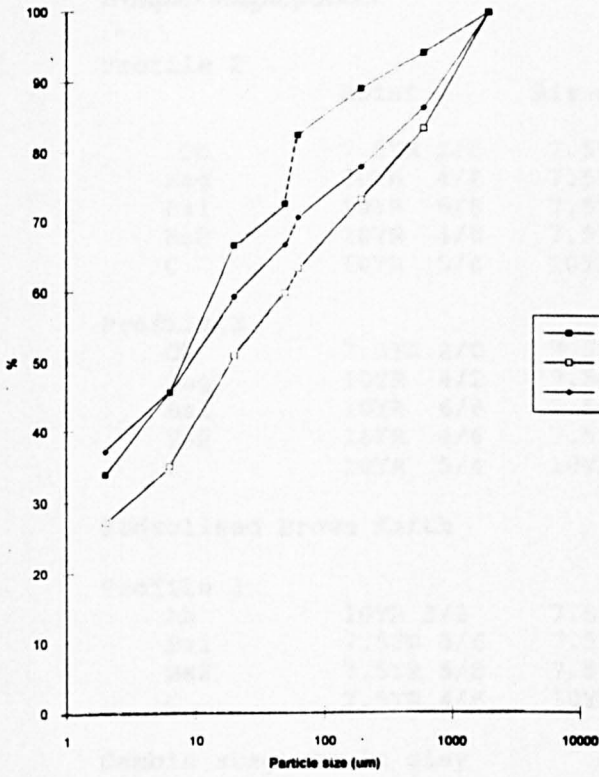
Appendix II d

Cumulative particle size distribution curves for a) ironpan stagnopodzol profiles b) brown podzolic soil profile c) stagnohumic gley soil profiles.

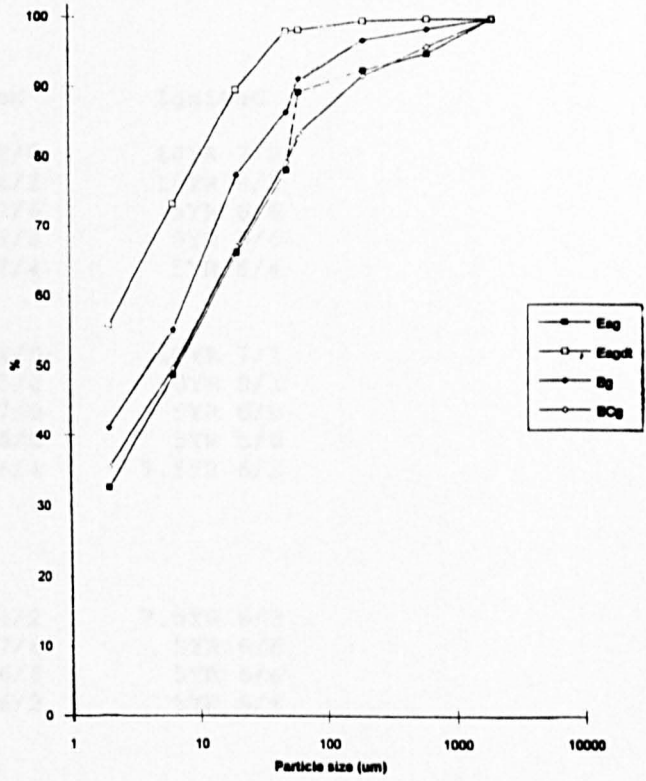


c)

p1



p2



Appendix IIe

Soil colour

Ironpan stagnopodzol

Profile 2

	Moist	Air-dried	Ignited
Oh	7.5YR 2/0	7.5YR 2/0	10YR 7/2
Eag	10YR 4/2	7.5YR 6/2	10YR 8/2
Bs1	10YR 6/8	7.5YR 7/6	5YR 6/6
Bs2	10YR 4/6	7.5YR 7/8	5YR 5/6
C	10YR 5/4	10YR 7/4	5YR 6/4

Profile 3

Oh	7.5YR 2/0	7.5YR 2/0	10YR 7/1
Eag	10YR 4/2	7.5YR 5/2	10YR 8/1
Bs1	10YR 6/8	7.5YR 7/6	5YR 6/6
Bs2	10YR 4/6	7.5YR 6/6	5YR 5/6
C	10YR 5/4	10YR 6/4	7.5YR 6/3

Podzolised Brown Earth

Profile 1

Ah	10YR 3/2	7.5YR 4/2	7.5YR 6/3
Bs1	7.5YR 5/6	7.5YR 7/6	5YR 6/6
Bs2	7.5YR 5/8	7.5YR 6/6	5YR 6/6
C	7.5YR 4/6	10YR 6/3	5YR 5/6

Cambic stagnohumic gley

Profile 2

Oh	7.5YR 2/0	7.5YR 3/0	10YR 7/3
Eag	10YR 3/3	10YR 6/3	7.5YR 8/3
Bg	10YR 5/1	10YR 7/1	7.5YR 7/3
BCg	10YR 6/1	10YR 7/1	7.5YR 7/2

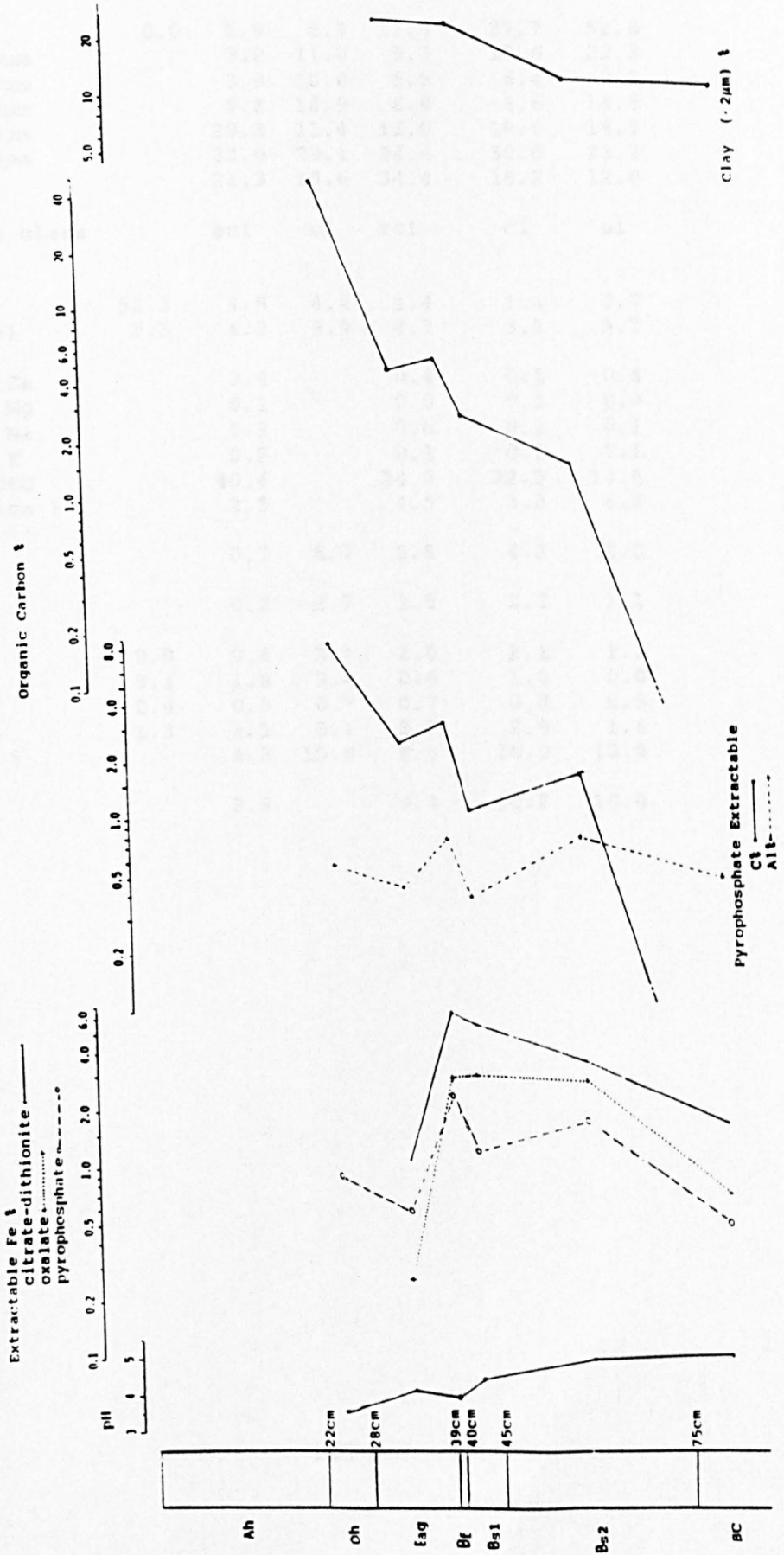
Appendix : If Physical and chemical data

a) ironpan stagnopodzolic profiles

a) Profile 1.

	Oh	Eag	Bf	Bs1	Bs2	BC
Stones >2mm		0.7	2.6	9.8	64.0	68.4
Sand 630-2000µm		10.1	12.0	10.7	20.9	38.2
200- 630µm		3.4	9.4	7.4	14.7	21.1
63- 200µm		3.3	21.2	5.8	8.6	10.1
Silt 20- 63µm		29.2	10.0	15.5	15.2	2.0
2- 20µm		28.6	27.5	36.0	24.3	16.8
Clay <2µm		25.4	20.0	24.6	16.4	11.8
Particle size class (SSEW)		scl	cl	cl	szl	sl
Organic C %	46.5	4.7	5.1	2.5	1.5	0.0
pH (H ₂ O 1:2.5)	3.5	4.1	3.9	4.3	4.8	4.9
Exchangeable Ca		0.4		0.4	0.6	0.4
Mg		0.2		0.0	0.1	0.1
Na		0.5		0.5	1.1	1.2
K		0.2		0.1	0.2	0.1
CEC		40.1		25.2	21.8	11.5
Base saturation %		2.7		4.2	4.5	6.1
Fe _d %		1.0	6.5	5.4	3.4	1.6
Fe _o %		0.2	2.5	2.9	2.7	0.8
Fe _p %	0.9	0.6	2.2	1.1	1.7	0.5
C _p %	8.5	2.5	3.1	1.0	1.8	0.0
Al _p %	0.6	0.5	0.8	0.4	0.8	0.5
Fe + Al %	1.5	1.1	3.0	1.5	2.5	1.0
Fe + Al/clay %		3.9	15.0	6.2	20.0	8.2
pH (NaF)		9.0		9.4	10.2	10.0

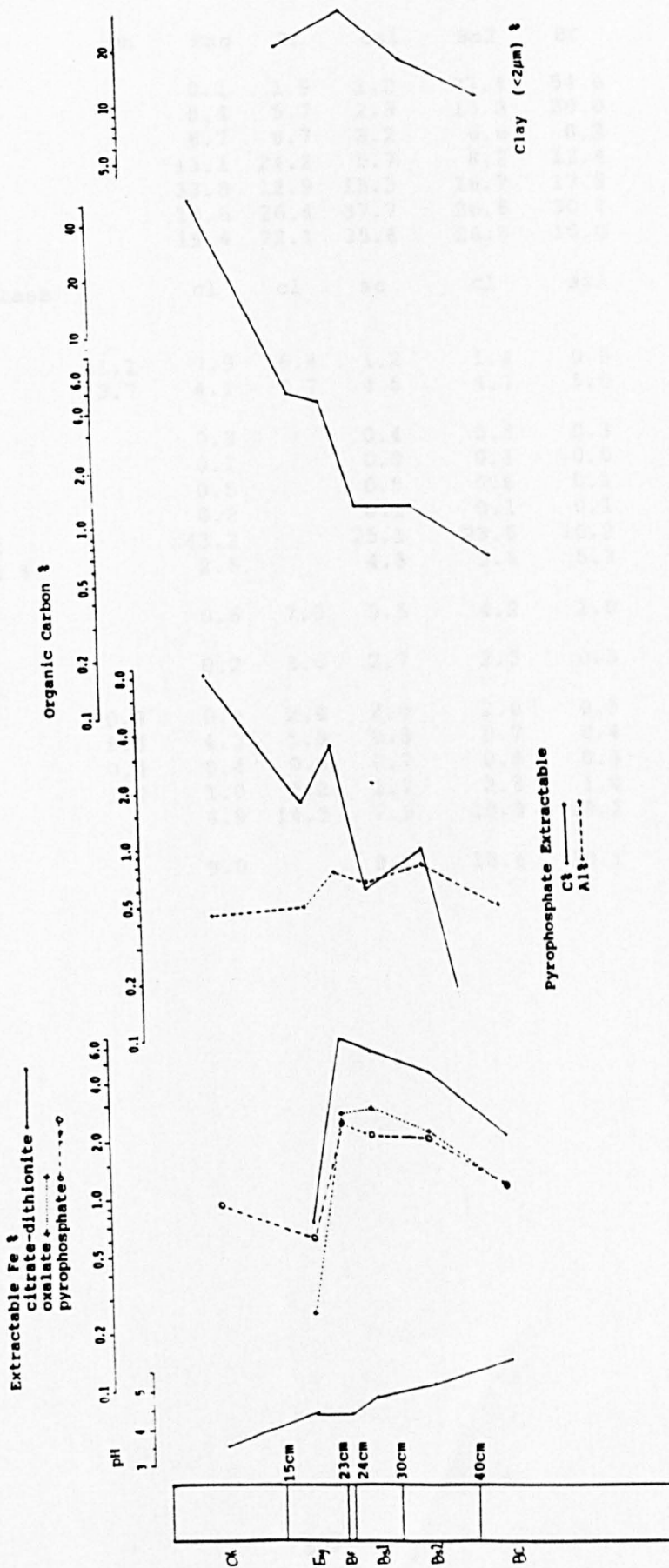
Graphic representation of the physical and chemical data for an ironpan stagnopodzolic profile (P1).



Profile 2

	Oh	Eag	Bf	Bs1	Bs2	BC
Stones >2mm	0.0	5.9	8.9	11.5	37.7	52.6
Sand 630-2000µm		3.2	11.0	5.7	17.6	22.3
200- 630µm		3.8	10.0	5.5	6.4	9.3
63- 200µm		9.8	18.9	6.8	8.6	14.6
Silt 20- 63µm		29.3	11.4	13.0	18.6	18.5
2- 20µm		32.6	29.1	34.6	30.6	23.2
Clay <2µm		21.3	19.6	34.4	18.2	12.0
Particle size class (SSEW)		scl	cl	zcl	cl	sl
Organic C %	52.3	4.9	4.4	1.4	1.4	0.7
pH (H ₂ O 1:2.5)	3.5	4.3	3.9	4.7	5.1	5.7
Exchangeable Ca		0.4		0.4	0.5	0.4
Mg		0.1		0.0	0.1	0.0
Na		0.3		0.6	0.2	0.1
K		0.2		0.1	0.1	0.1
CEC		40.4		24.8	22.5	10.6
Base saturation %		2.5		4.5	3.8	6.2
Fe _d %		0.7	6.7	5.5	4.2	2.0
Fe _o %		0.2	2.7	2.8	2.2	1.1
Fe _p %	0.9	0.6	2.4	2.0	2.1	1.1
C _p %	8.1	1.8	3.4	0.6	1.0	0.0
Al _p %	0.4	0.5	0.7	0.7	0.8	0.5
Fe + Al %	1.3	1.1	3.1	2.7	2.9	1.6
Fe + Al/clay %		4.3	15.8	8.0	16.0	13.9
pH (NaF)		8.9		9.4	10.2	10.0

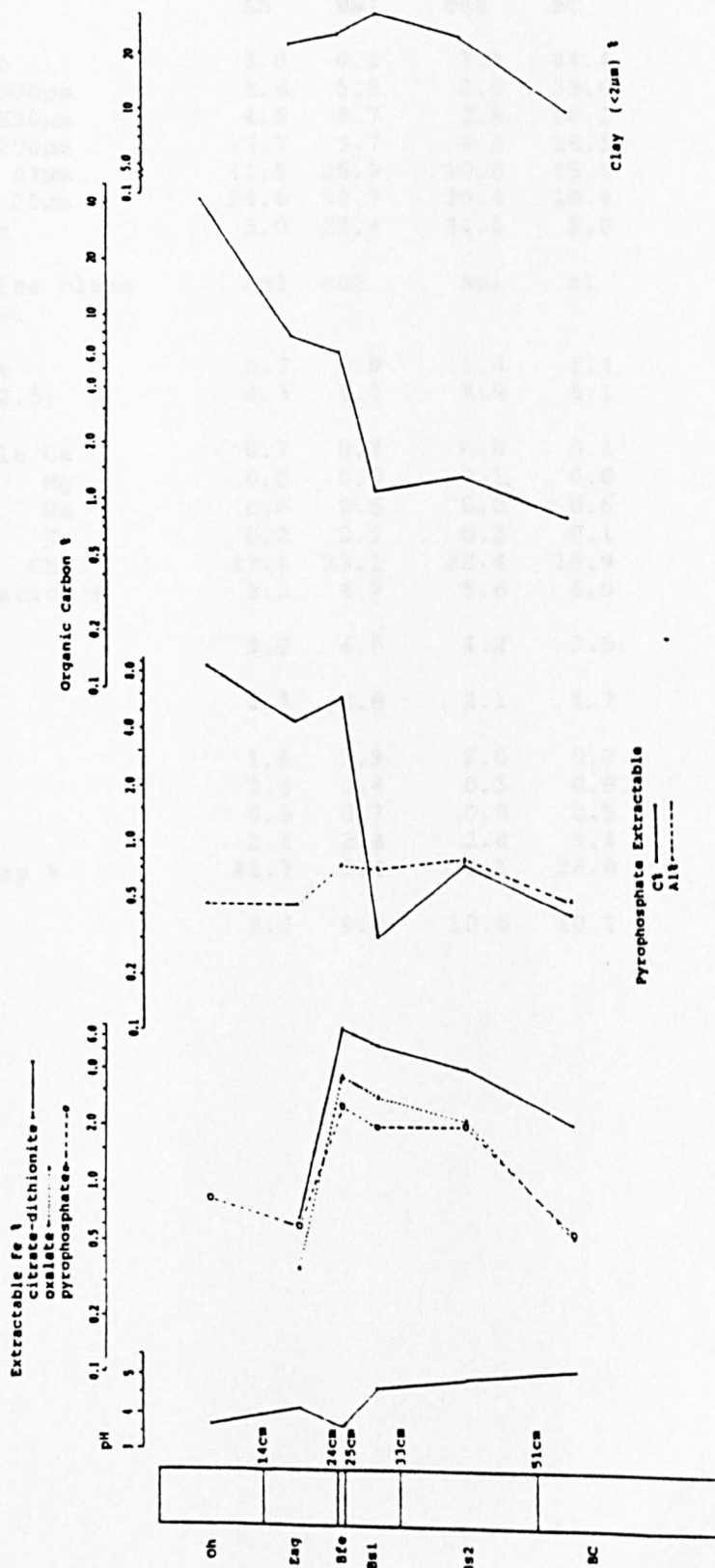
Graphic representation of the physical and chemical data for an ironpan stagnopodzolic profile (P2).



Profile 3.

	Oh	Eag	Bf	Bs1	Bs2	BC
Stones >2mm		0.1	1.9	1.2	27.4	54.6
Sand 630-2000µm		8.4	5.7	2.3	15.3	20.0
200- 630µm		6.7	8.7	3.2	6.6	8.2
63- 200µm		13.1	24.2	5.7	8.2	13.4
Silt 20- 63µm		33.8	12.9	15.5	16.7	17.9
2- 20µm		18.6	26.4	37.7	26.6	30.4
Clay <2µm		19.4	22.1	35.6	26.5	10.0
Particle size class (SSEW)		cl	cl	sc	cl	szl
Organic C %	41.1	7.9	6.4	1.2	1.4	0.9
pH (H ₂ O 1:2.5)	3.7	4.1	3.7	4.5	4.7	5.0
Exchangeable Ca		0.3		0.4	0.5	0.3
Mg		0.1		0.0	0.1	0.0
Na		0.5		0.5	0.6	0.1
K		0.2		0.1	0.1	0.1
CEC		43.2		25.1	23.6	10.2
Base saturation %		2.5		4.3	5.6	5.3
Fe _d %		0.6	7.0	5.5	4.2	2.0
Fe _o %		0.2	3.6	2.7	2.3	0.5
Fe _p %	0.8	0.6	2.4	2.0	2.0	0.5
C _p %	8.4	4.3	5.8	0.3	0.7	0.4
Al _p %	0.4	0.4	0.8	0.7	0.8	0.5
Fe ⁺ + Al %	1.2	1.0	3.2	2.7	2.8	1.0
Fe + Al/clay %		4.9	14.5	7.6	10.8	10.1
pH (NaF)		9.0		9.6	10.4	10.1

Graphic representation of the physical and chemical data for an ironpan stagnopodzolic profile (P3).

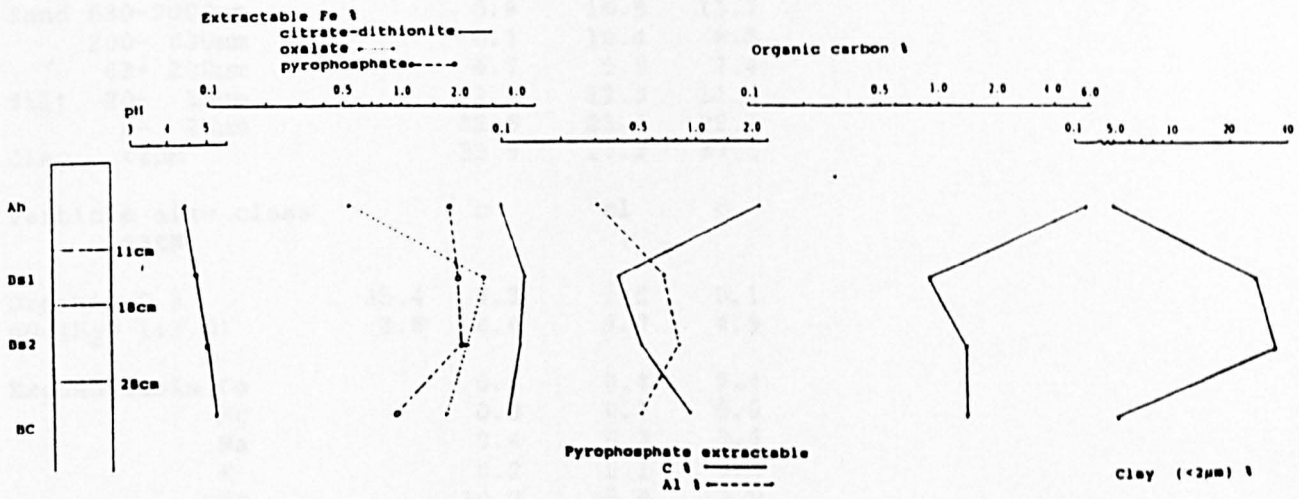


b) brown podzolic soil profile

Profile 1.

	Ah	Bs1	Bs2	BC
Stones >2mm	3.8	0.2	1.3	64.4
Sand 630-2000µm	6.6	5.8	2.5	33.6
200- 630µm	4.5	3.7	2.8	10.2
63- 200µm	17.7	3.7	4.5	16.5
Silt 20- 63µm	41.5	20.9	20.0	15.3
2- 20µm	24.6	38.7	35.6	19.4
Clay <2µm	5.0	27.4	34.5	5.0
Particle size class (SSEW)	sz1	zcl	zcl	sl
Organic C %	5.7	0.9	1.4	1.4
pH (H ₂ O 1:2.5)	4.3	4.7	4.9	5.1
Exchangeable Ca	0.7	0.7	0.8	0.4
Mg	0.2	0.0	0.1	0.0
Na	0.6	0.6	0.2	0.6
K	0.2	0.1	0.2	0.1
CEC	47.4	23.1	22.4	18.9
Base saturation %	3.5	6.2	5.6	6.0
Fe _d %	3.2	4.5	4.2	3.5
Fe _o %	0.5	2.6	2.1	1.7
Fe _p %	1.8	1.9	2.0	0.9
C _p %	2.4	0.4	0.5	0.9
Al _p %	0.3	0.7	0.8	0.5
Fe + Al %	2.1	2.6	2.8	1.4
Fe + Al/clay %	41.7	9.4	8.1	28.0
pH (NaF)	8.6	9.6	10.6	10.1

Graphic representation of the physical and chemical data for a brown podzolic soil profile.

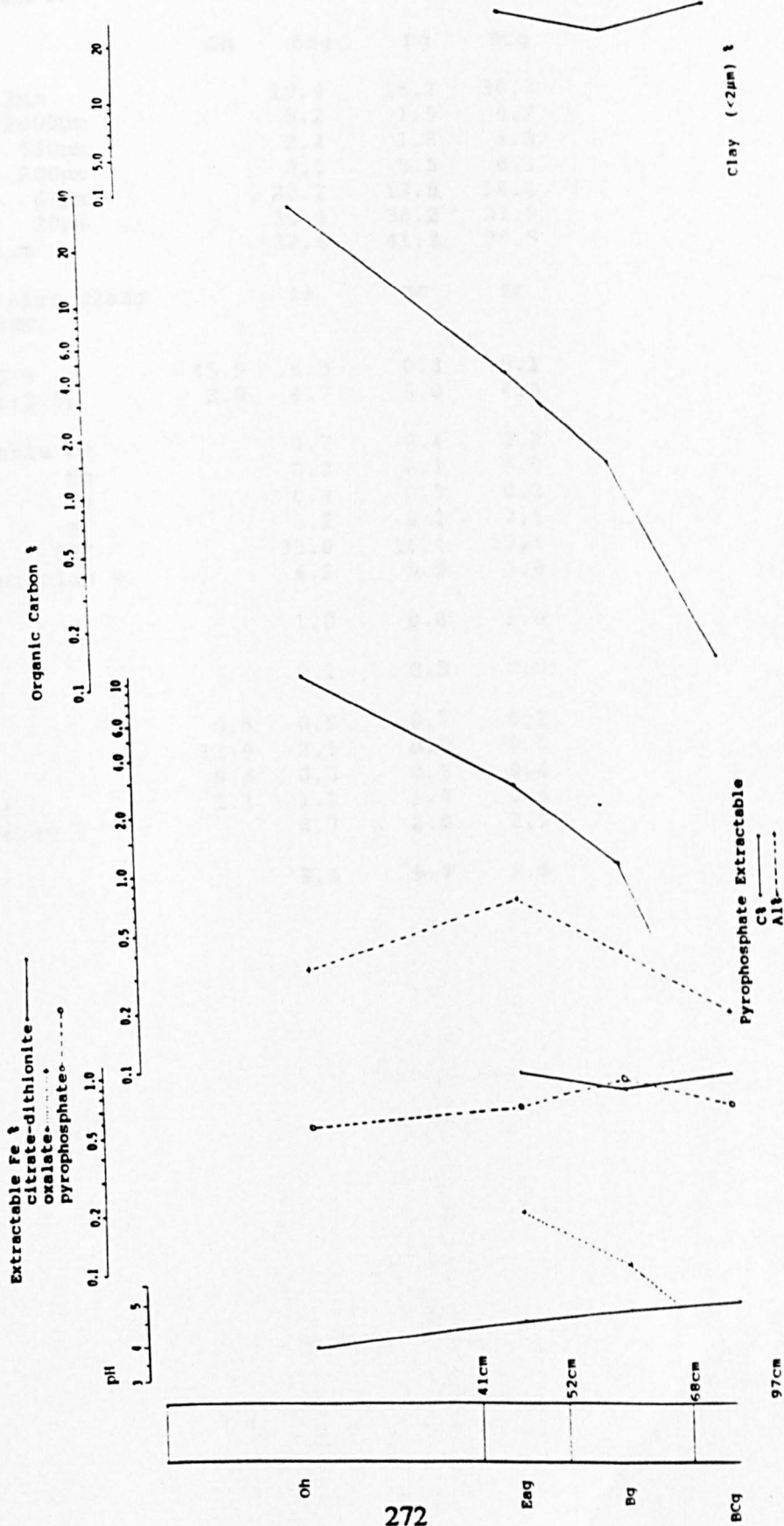


c) Stagnohumic gley soil profiles.

Profile 1.

	Oh	Eag	Bg	BCg
Stones >2mm		1.1	5.1	49.4
Sand 630-2000µm		5.8	16.6	13.7
200- 630µm		5.1	10.4	8.5
63- 200µm		6.7	9.9	7.4
Silt 20- 63µm		11.2	12.3	11.2
2- 20µm		32.6	23.6	22.1
Clay <2µm		33.9	27.2	37.1
Particle size class (SSEW)		c	cl	c
Organic C %	35.4	4.3	1.5	0.1
pH (H ₂ O 1:2.5)	3.8	4.4	4.7	4.9
Exchangeable Ca		0.6	0.4	0.4
Mg		0.3	0.1	0.0
Na		0.4	0.3	0.4
K		0.2	0.1	0.1
CEC		30.2	15.8	13.0
Base saturation %		4.9	5.7	7.2
Fe _d %		1.0	0.8	1.0
Fe _o %		0.2	0.1	0.0
Fe _p %	0.6	0.7	1.0	0.8
C _p %	12.0	2.8	1.1	0.0
Al _p %	0.3	0.8	0.4	0.2
Fe + Al %	0.9	1.5	1.4	1.0
Fe + Al/clay %		4.3	4.9	2.7
pH (NaF)		9.4	9.8	9.7

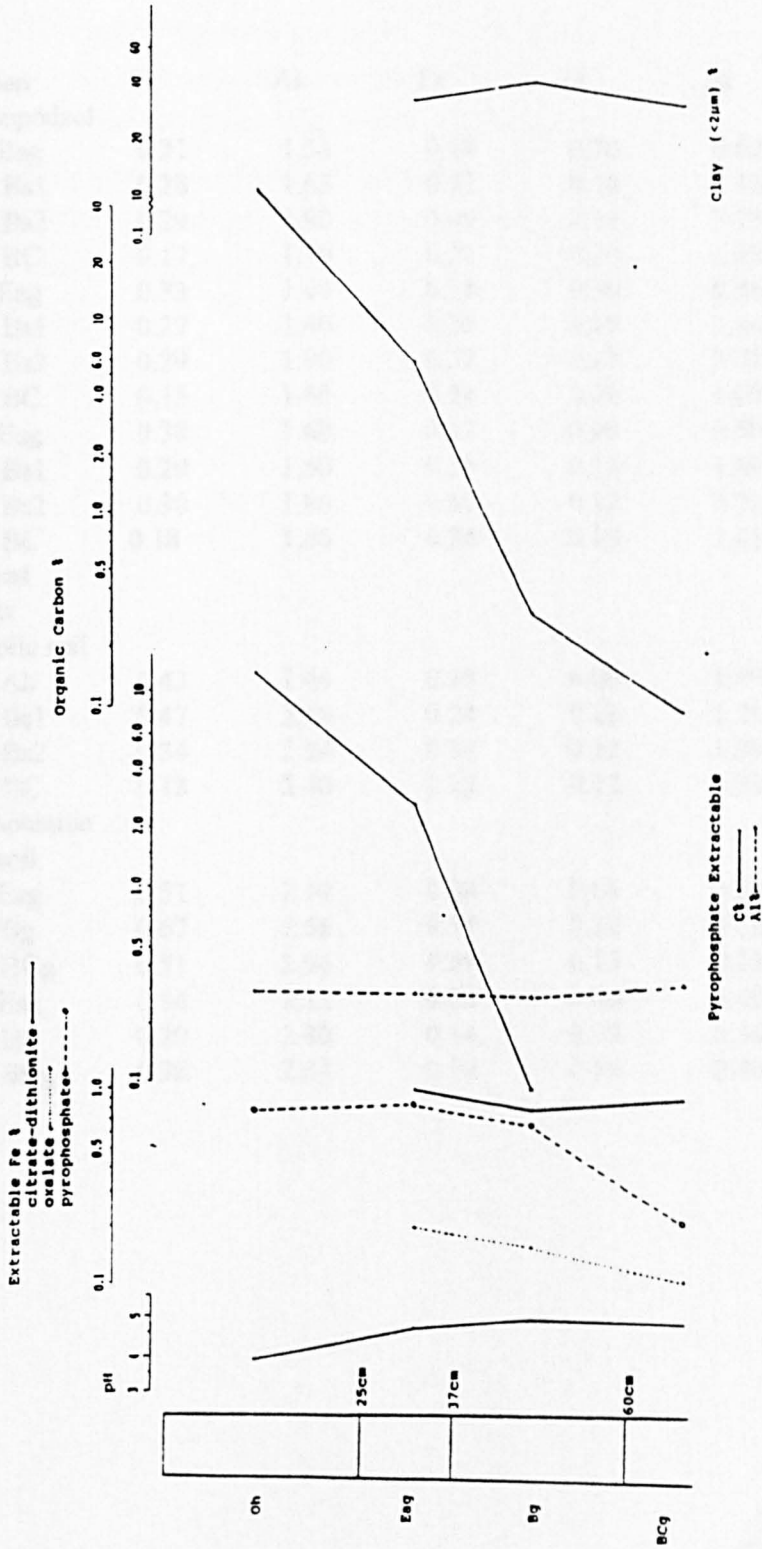
Graphic representation of the physical and chemical data for a stagnohumic gley soil profile (P1).



Profile 2.

	Oh	Eag	Bg	BCg
Stones >2mm		10.4	15.2	30.3
Sand 630-2000µm		5.2	1.5	4.2
200- 630µm		2.4	1.8	4.3
63- 200µm		3.1	5.5	8.1
Silt 20- 63µm		23.2	13.8	16.4
2- 20µm		33.5	36.2	31.5
Clay <2µm		32.6	41.2	35.5
Particle size class (SSEW)		zl	zc	zc
Organic C %	45.9	6.3	0.3	0.1
pH (H ₂ O 1:2.5)	3.9	4.7	5.0	4.9
Exchangeable Ca		0.7	0.4	0.3
Mg		0.2	0.1	0.0
Na		0.4	0.3	0.3
K		0.2	0.1	0.1
CEC		35.8	16.4	12.1
Base saturation %		4.2	5.9	5.9
Fe _d %		1.0	0.8	1.0
Fe _o %		0.1	0.3	0.0
Fe _p %	0.8	0.9	0.7	0.2
C _p %	11.9	2.5	0.0	0.0
Al _p %	0.3	0.3	0.3	0.4
Fe + Al %	1.1	1.2	1.0	0.6
Fe + Al/clay %		3.7	2.5	1.1
pH (NaF)		9.4	9.7	9.8

Graphic representation of the physical and chemical data for a stagnohumic gley soil profile (P2).



Appendix IIg

Extractable amorphous materials in soil clay fraction.

Sample	0.5N NaOH (%)			Dithionite-citrate (%)		
	Si	Al	Fe	Si	Al	Fe
Ironpan stagnopodzol						
P1 - Eag	0.21	1.54	0.18	0.20	0.62	0.32
Bs1	0.28	1.63	0.32	0.18	1.46	3.20
Bs2	0.29	1.90	0.49	0.14	3.75	8.90
BC	0.17	1.79	0.26	0.20	1.68	4.64
P2 - Eag	0.33	1.44	0.18	0.20	0.56	0.32
Bs1	0.27	1.40	0.30	0.15	1.46	3.20
Bs2	0.29	1.90	0.52	0.13	3.72	10.40
BC	0.15	1.60	0.24	0.20	1.69	5.28
P3 - Eag	0.38	1.60	0.17	0.20	0.50	0.48
Bs1	0.29	1.50	0.33	0.15	1.69	3.84
Bs2	0.30	1.86	0.50	0.12	3.72	10.08
BC	0.18	1.66	0.24	0.20	1.41	5.12
Typical brown podzolic soil						
Ah	0.43	1.44	0.18	0.06	1.69	11.20
Bs1	0.47	2.60	0.24	0.13	1.21	11.52
Bs2	0.34	2.24	0.30	0.12	1.30	11.52
BC	0.18	2.40	0.22	0.12	1.33	8.88
Stagnohumic gley soil						
P1 - Eag	0.51	2.14	0.08	0.06	0.50	0.64
Bg	0.67	2.66	0.14	0.20	0.52	2.00
BCg	0.51	2.94	0.09	0.15	0.53	0.80
P2 - Eag	0.34	2.12	0.08	0.06	0.40	0.64
Bg	0.29	2.80	0.14	0.10	0.36	2.40
BCg	0.38	2.84	0.09	0.16	0.40	0.88

Appendix III

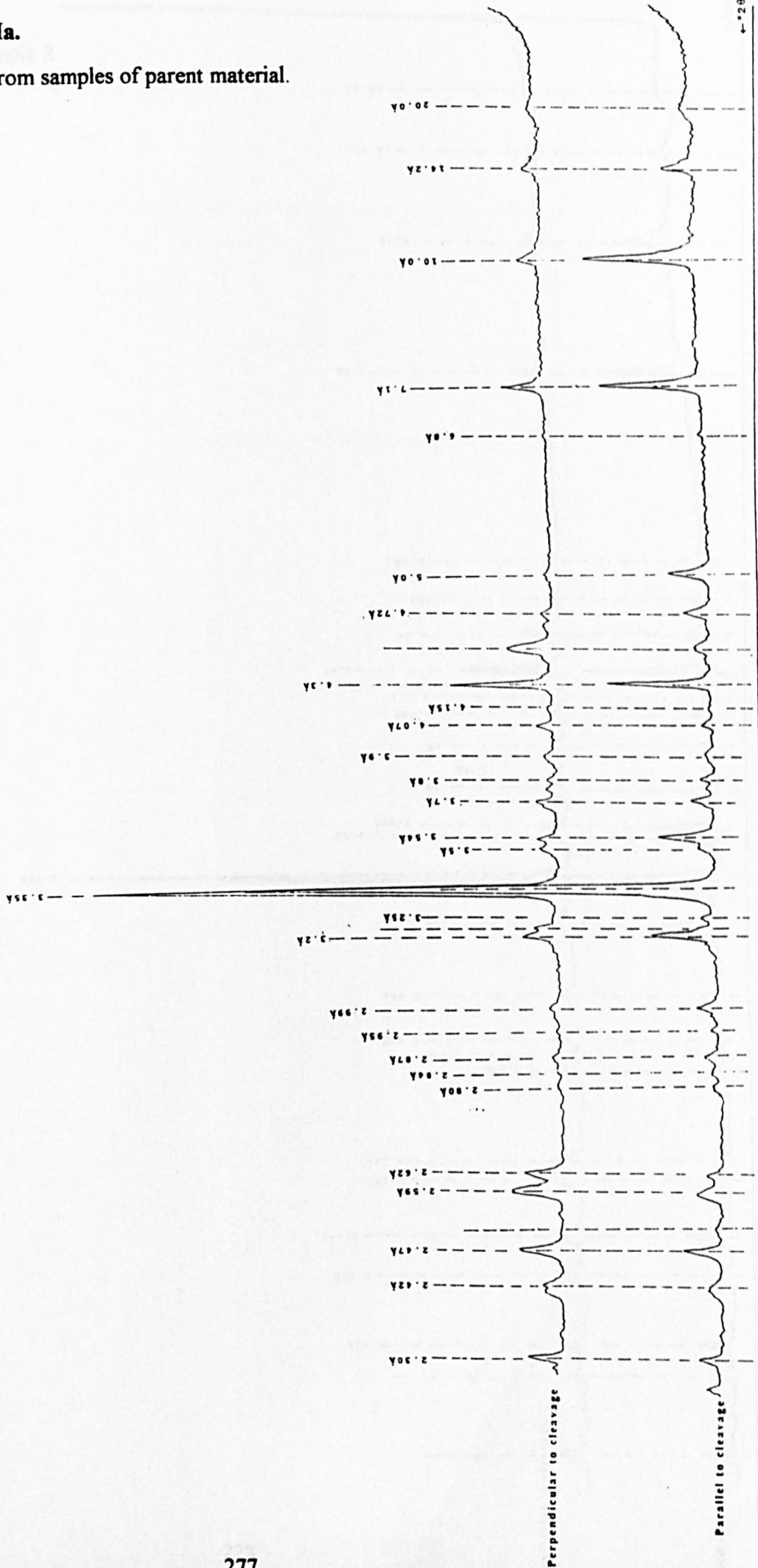
Clay mineralogy - X-ray diffraction traces of the clay fraction

- a XRD traces from samples of parent material.
- b XRD traces from an ironpan stagnopodzol (P3).
- c XRD traces for minerals separated magnetically.
- d XRD traces from a brown podzolic soil profile.
- e XRD traces from a staghomic gley soil profile (P2).
- f XRD traces from the clay fraction from minerogenic core materials.

Appendix IIIa.

XRD traces from samples of parent material.

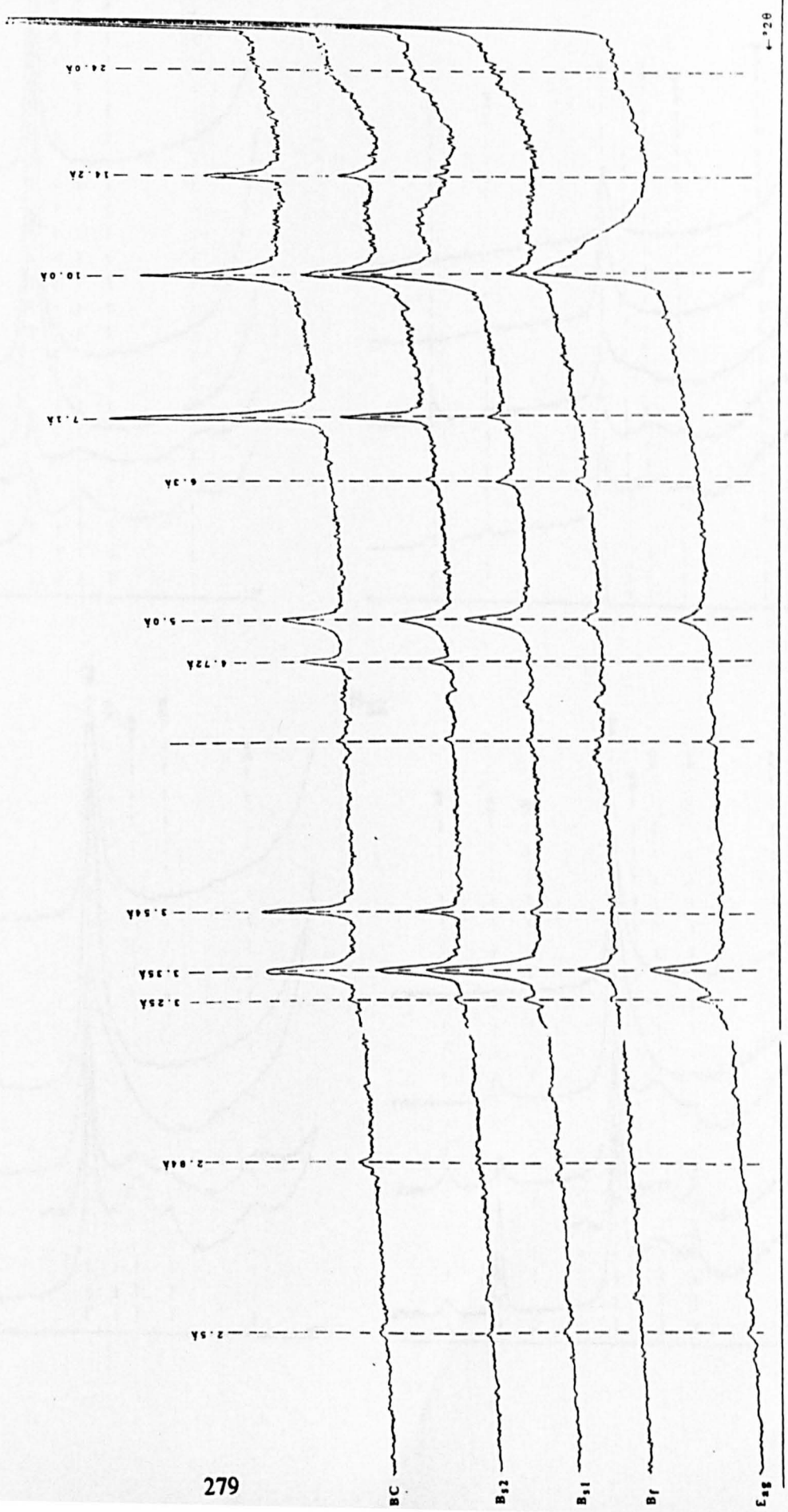
Sample 1



Appendix IIIb.

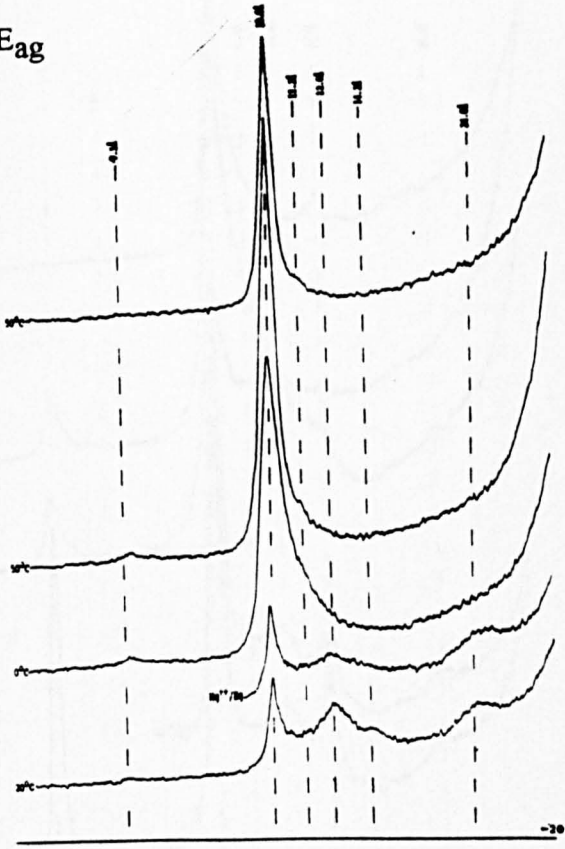
XRD traces from an ironpan stagnopodzol (P3; <2 μ m fraction).

1. Untreated samples

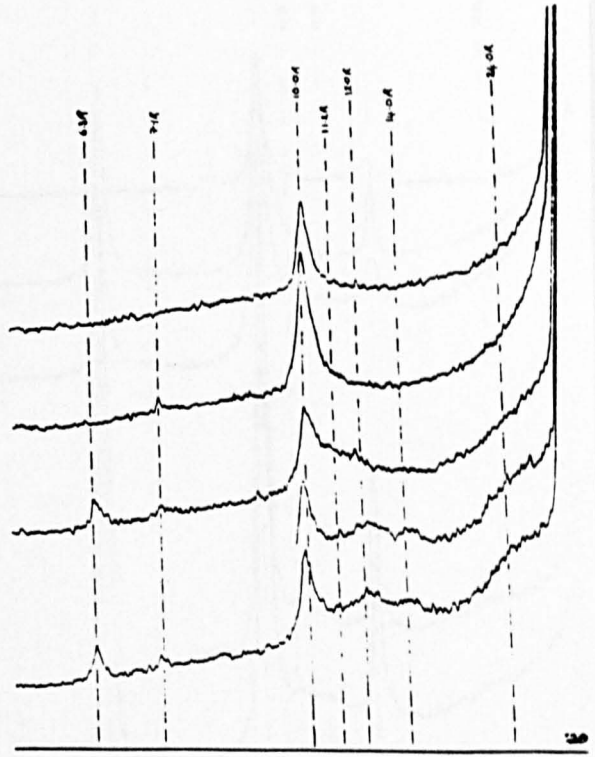


2. Samples treated with Mg^{++} and K^+ saturation

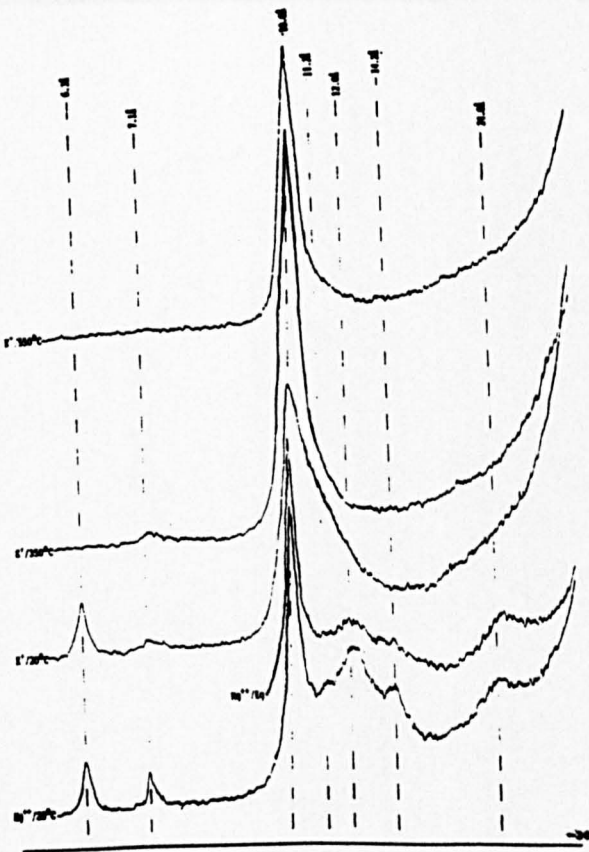
E_{ag}



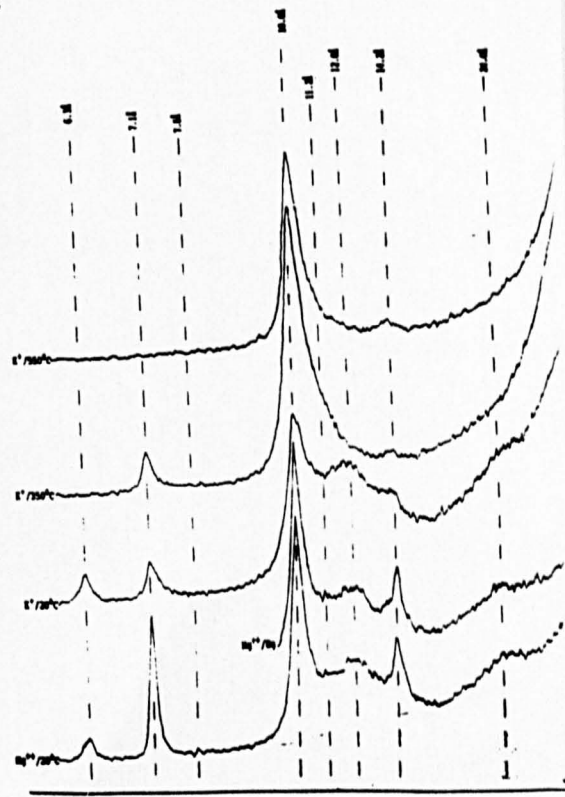
B_f



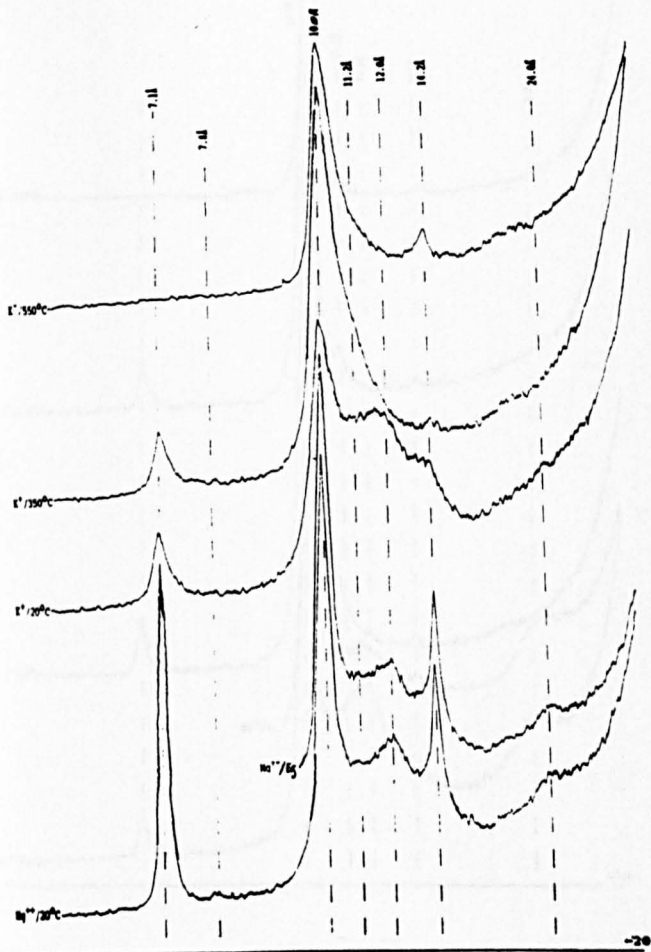
B_{S1}



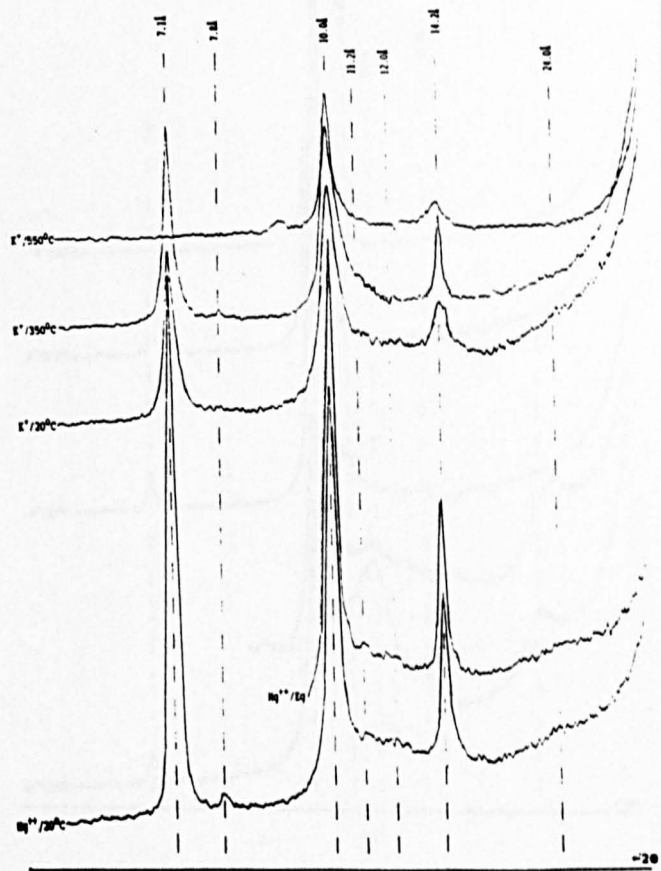
B_{S2}



B_s2DT

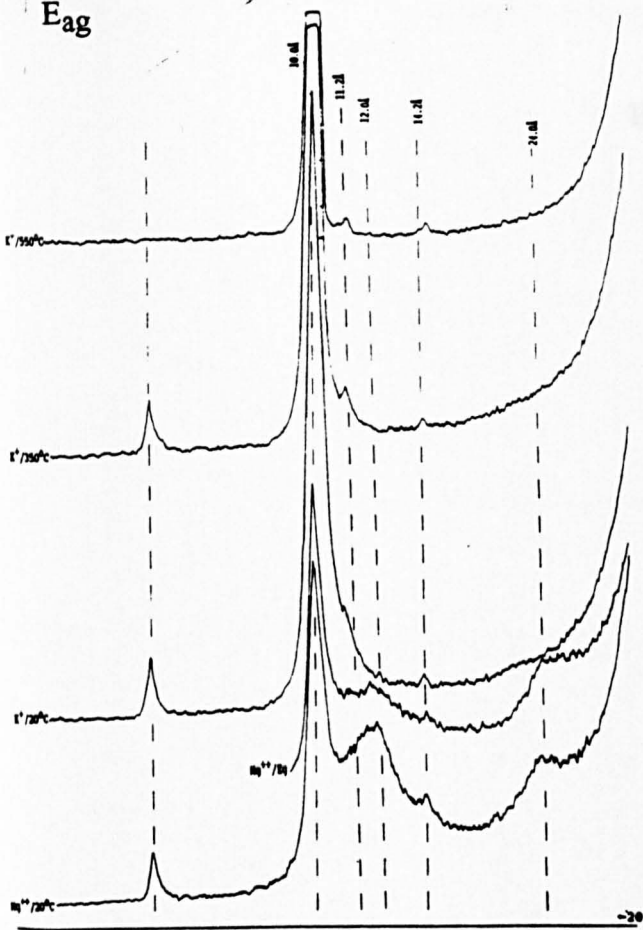


BC

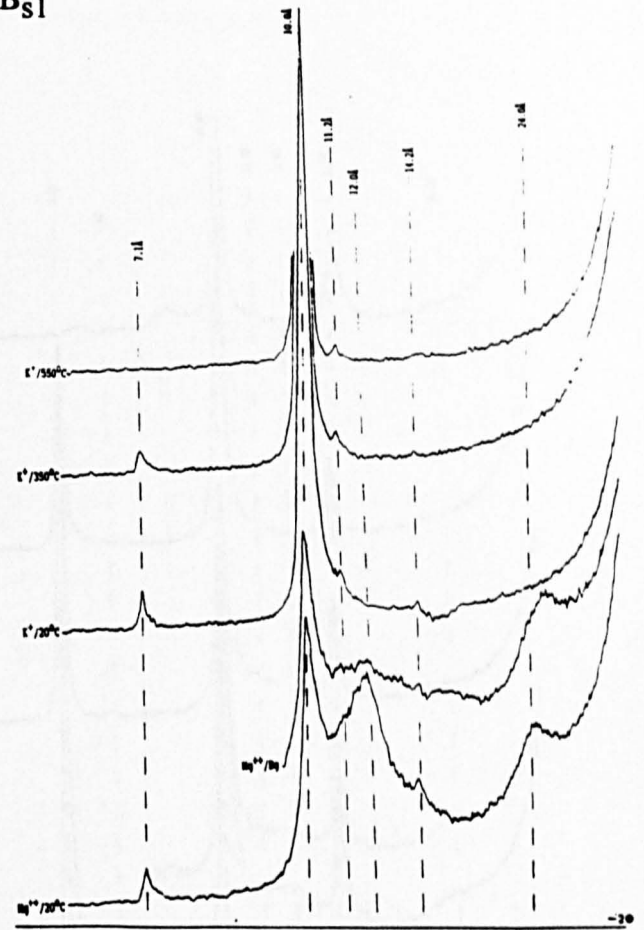


3. Samples cleaned with 0.5M NaOH and then saturated with Mg^{++} and K^+

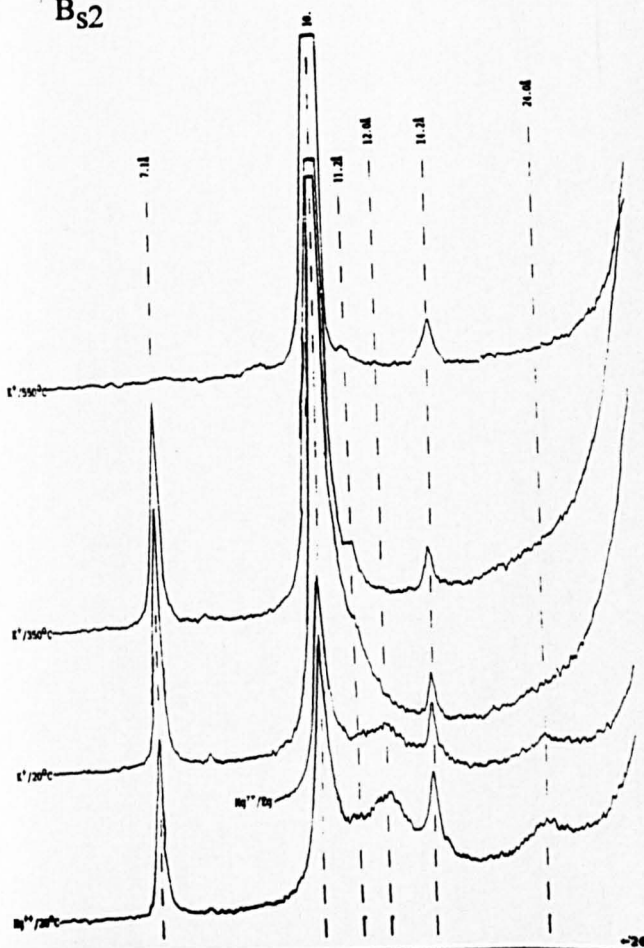
E_{ag}



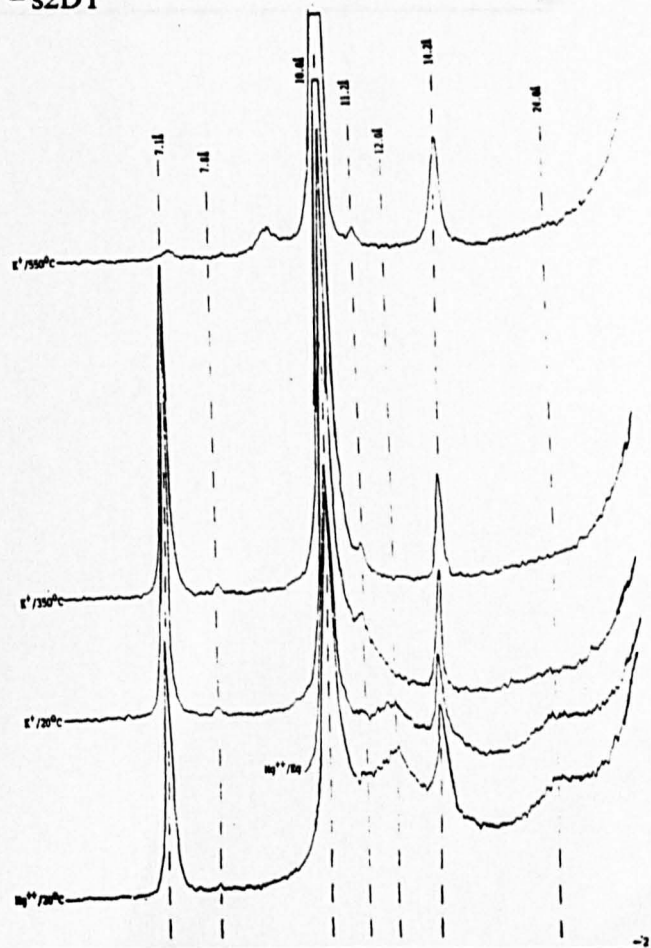
B_{s1}



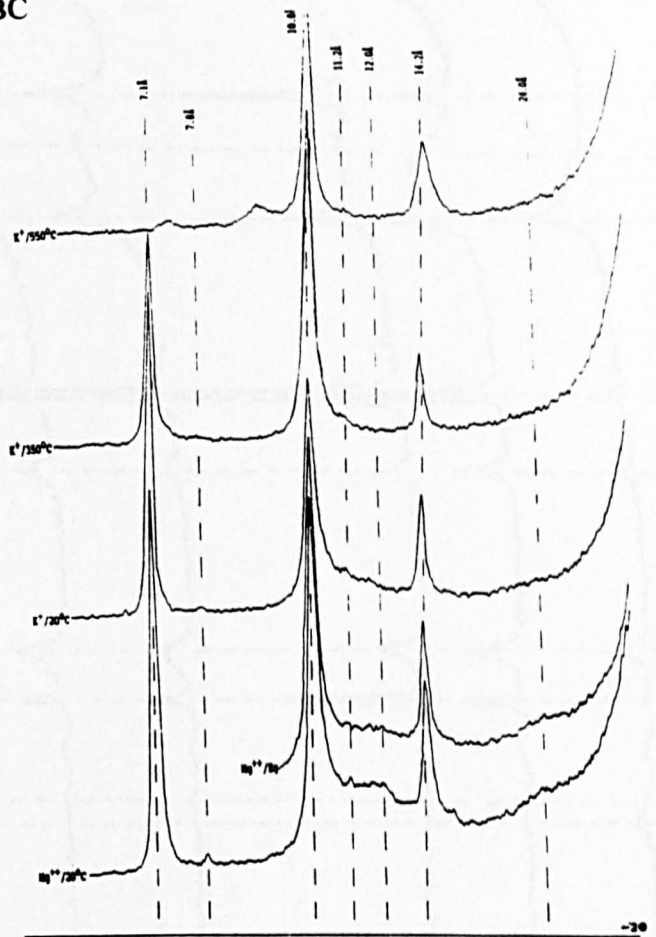
B_{s2}



B_{s2DT}

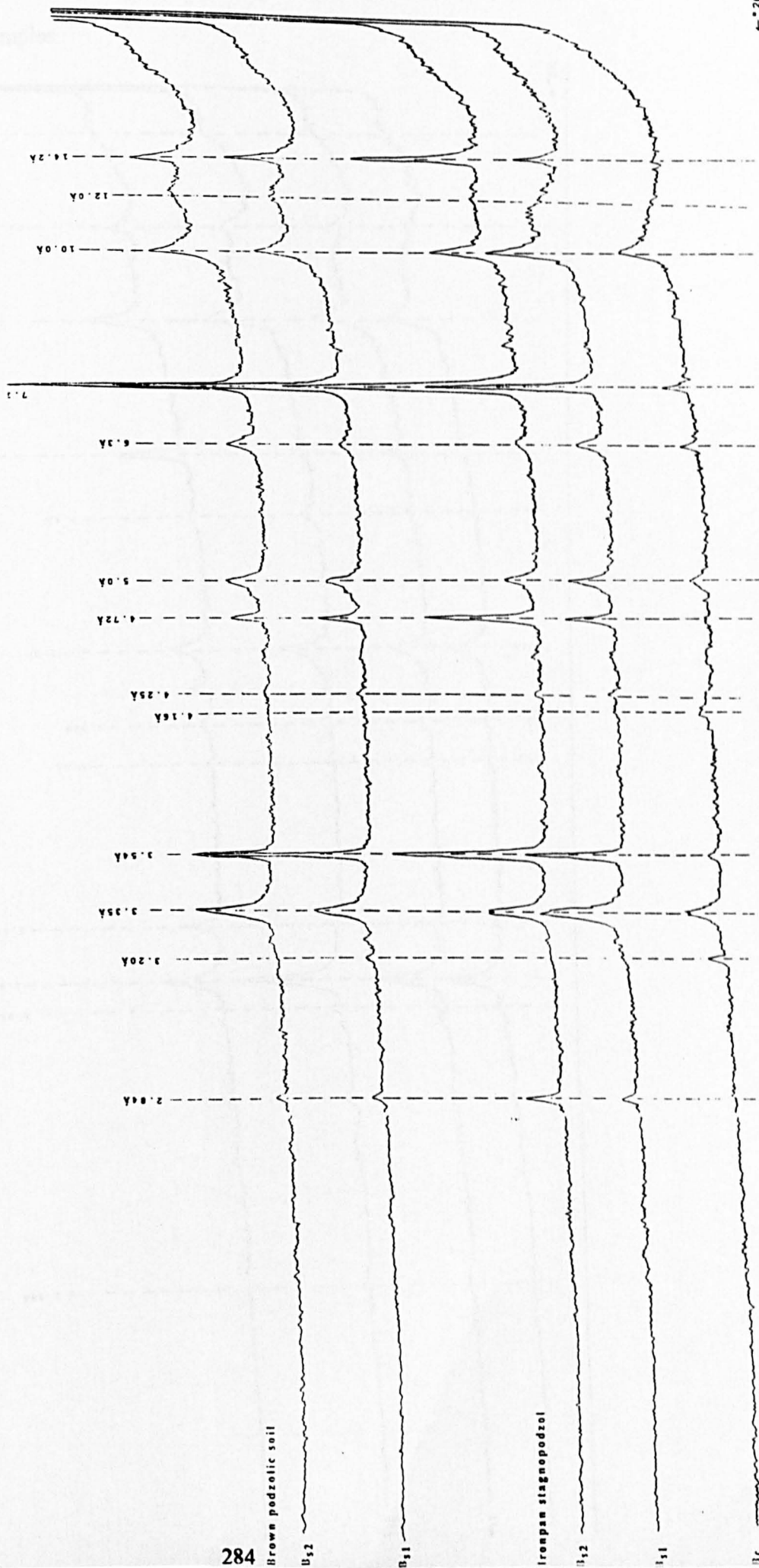


BC



Appendix IIIc

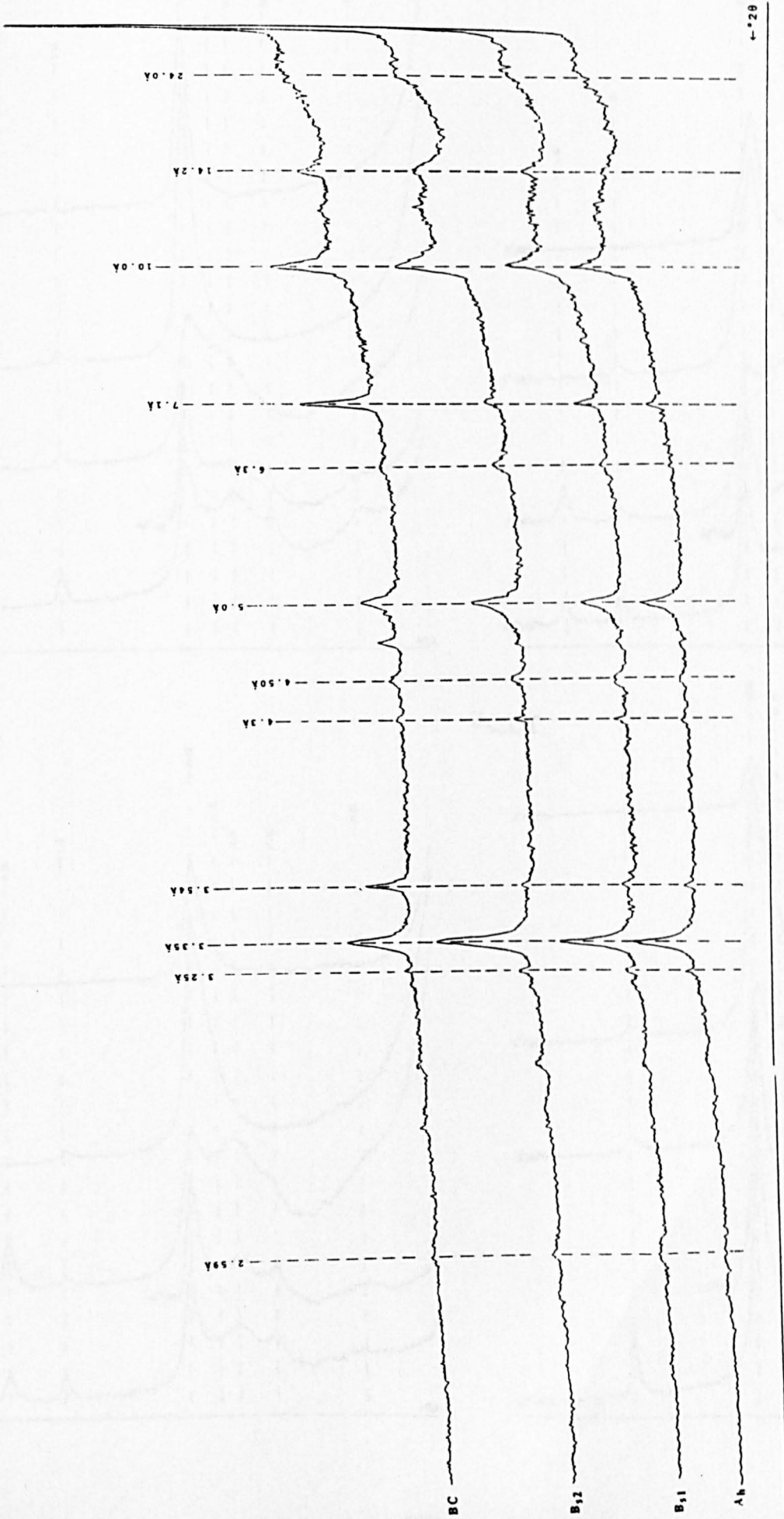
XRD traces for minerals extracted magnetically.



Appendix III d

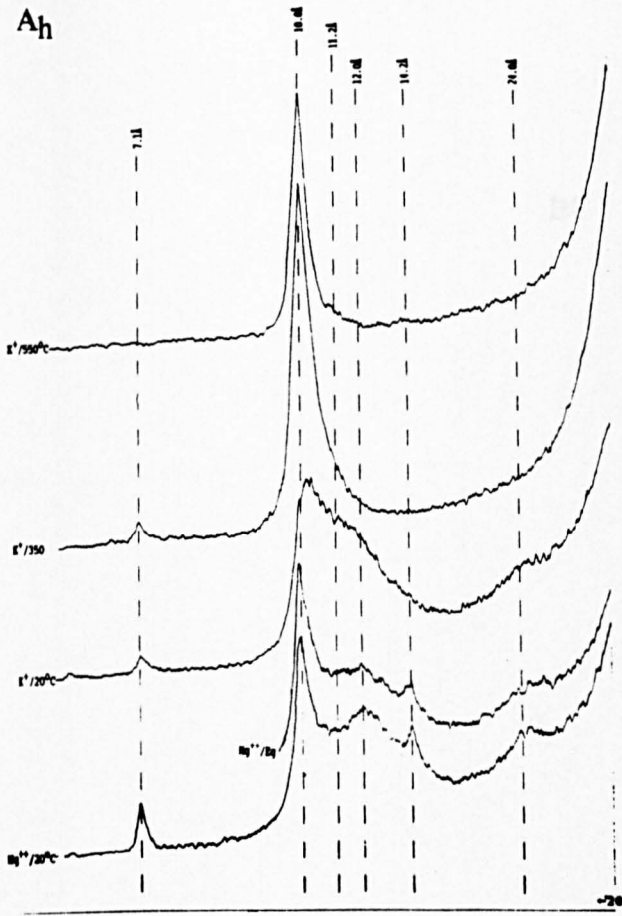
XRD traces from a brown podzolic soil profile (<2 μ m fraction).

1. Untreated samples

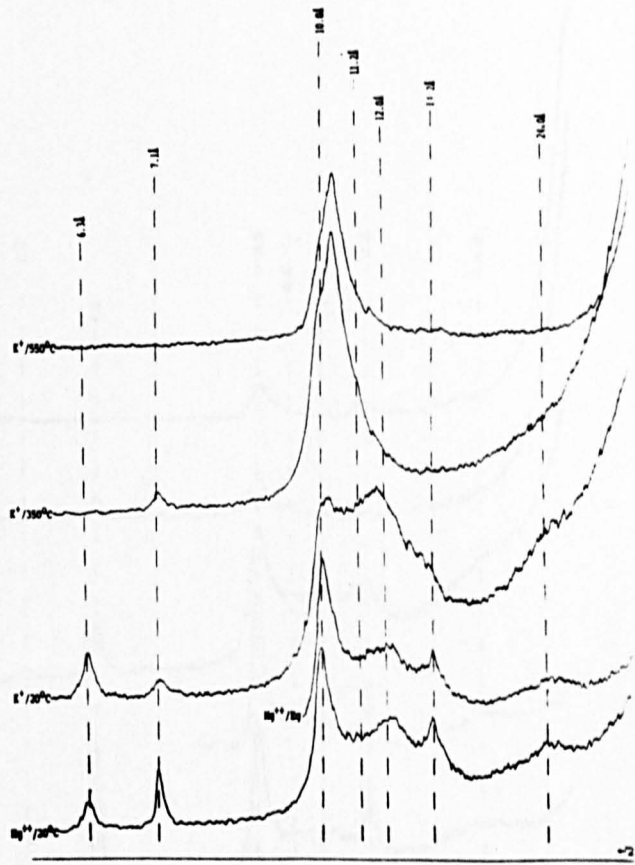


2. Samples treated with Mg^{++} and K^+ saturation

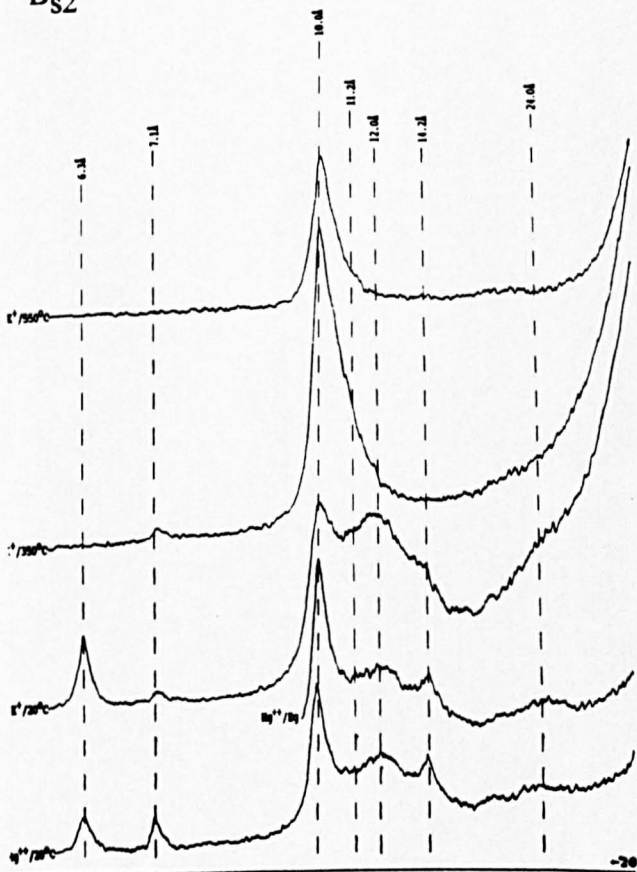
A_h



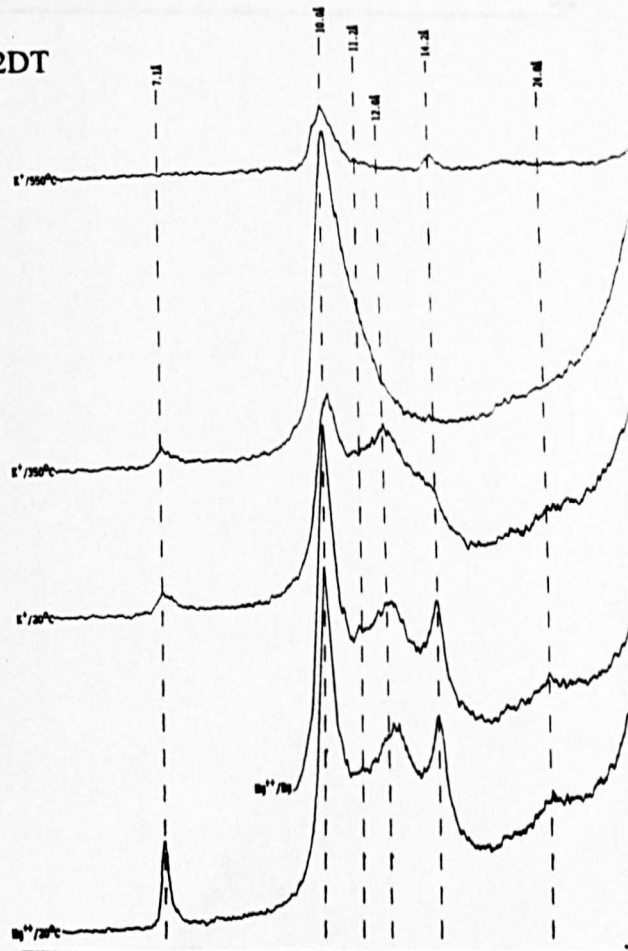
B_{S1}



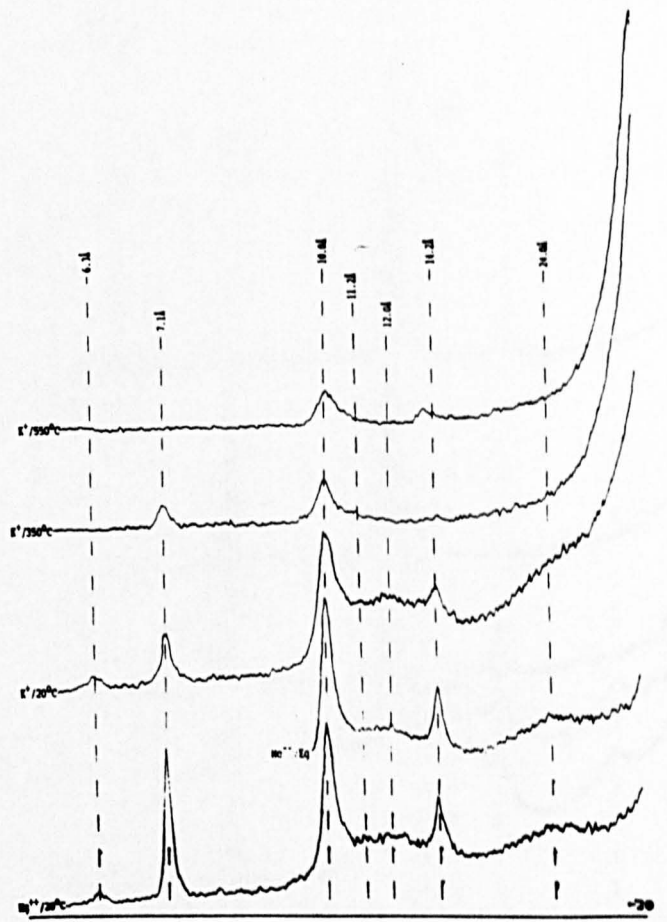
B_{S2}



B_{S2DT}

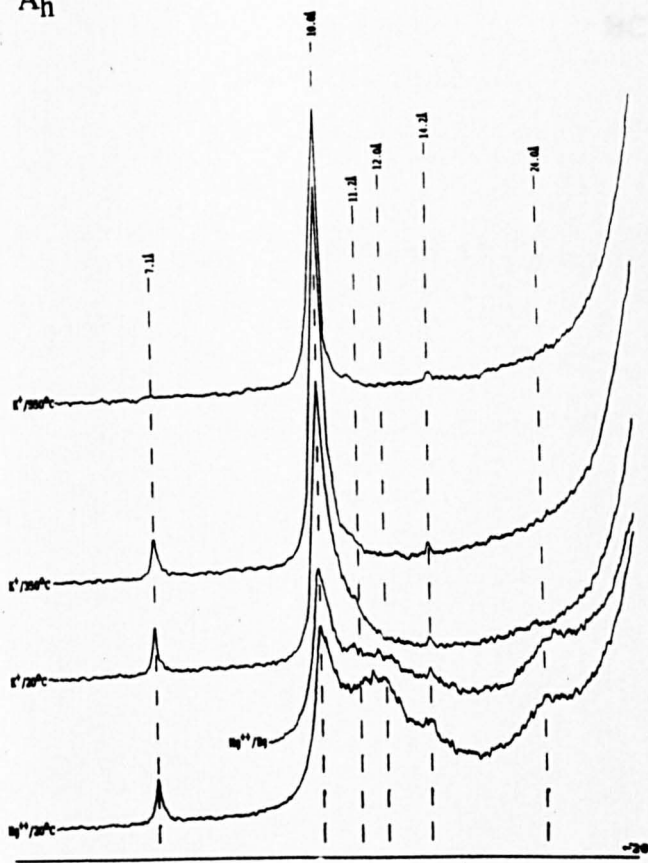


BC

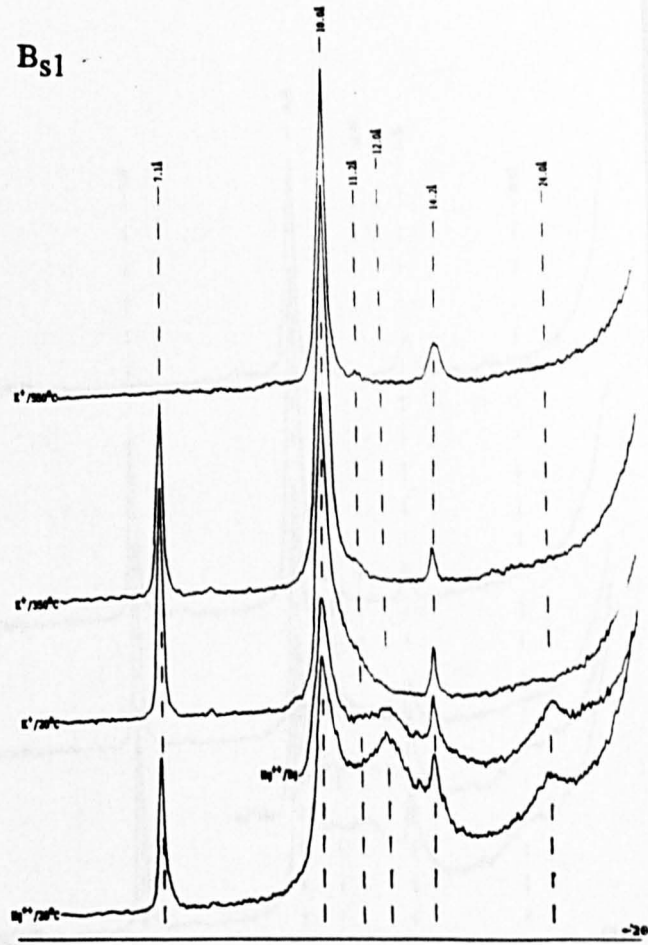


3. Samples cleaned with 0.5M NaOH and then saturated with Mg^{++} and K^+

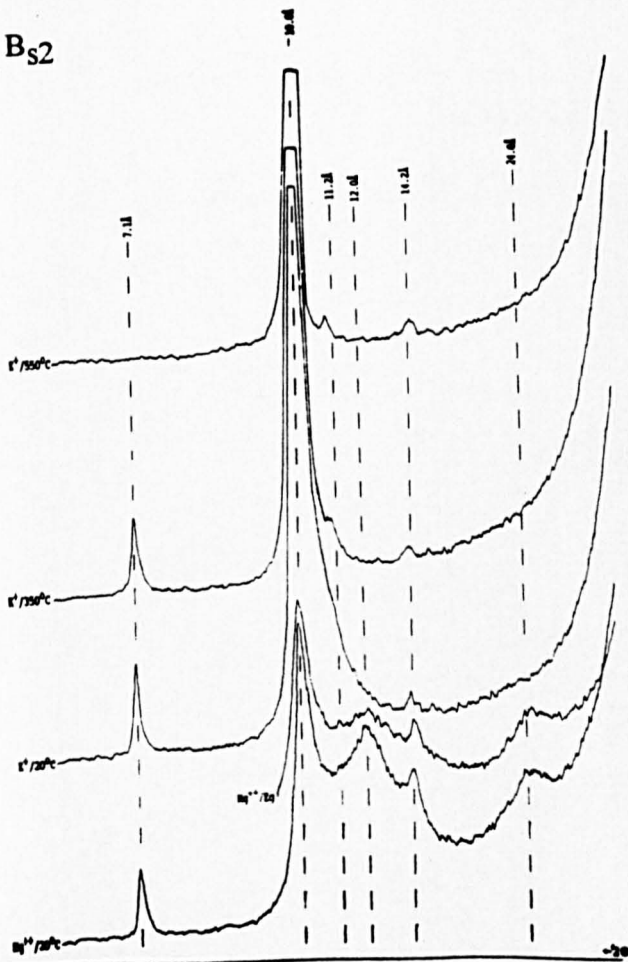
A_h



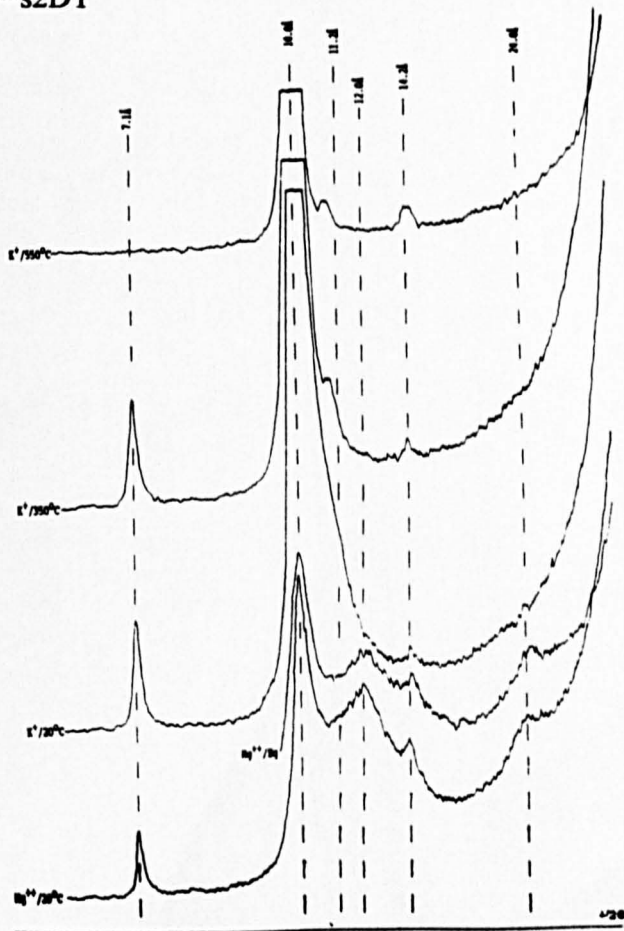
B_{s1}



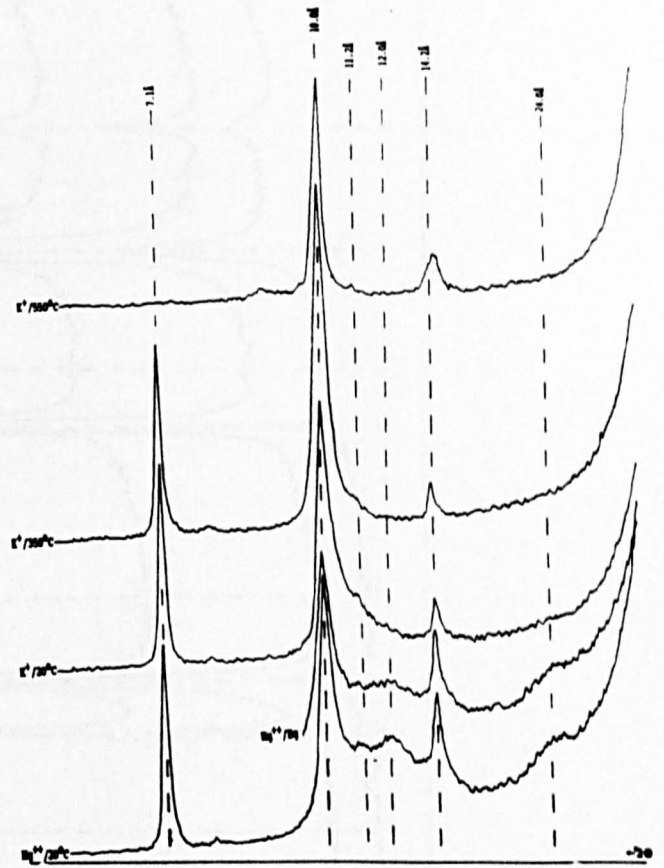
B_{s2}



B_{s2DT}



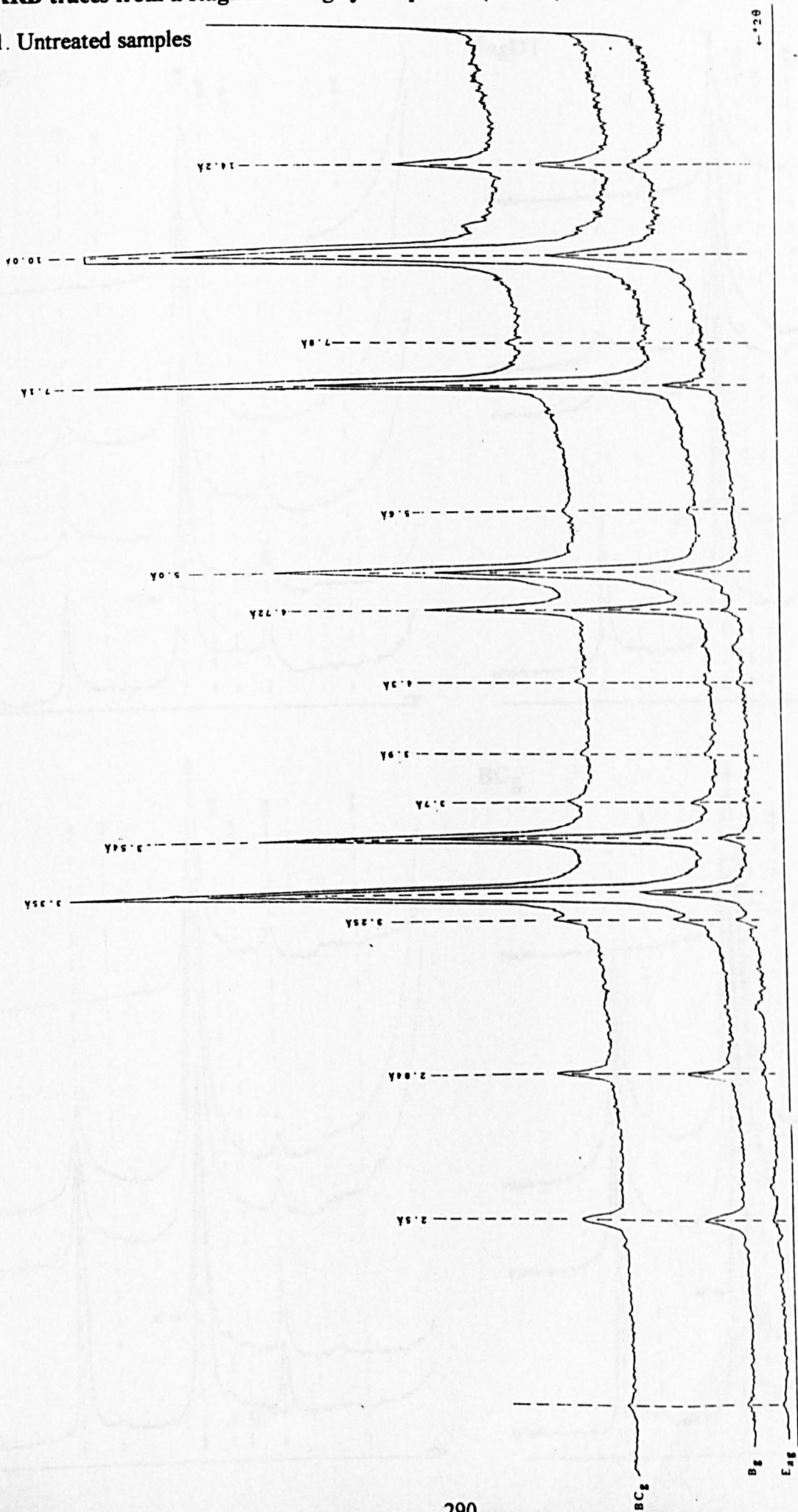
BC



Appendix IIIe

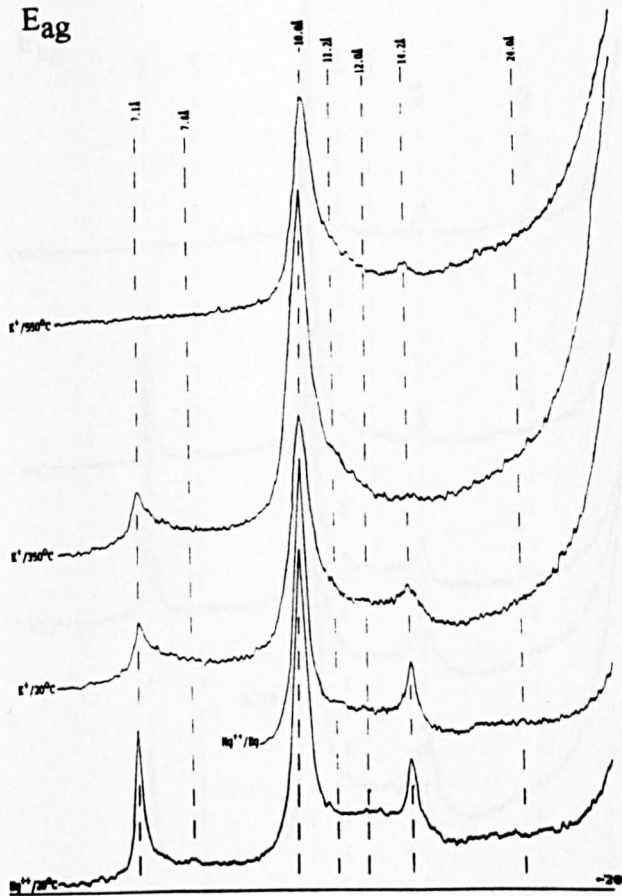
XRD traces from a stagnohumic gley soil profile (P2; <2 μ m fraction).

1. Untreated samples

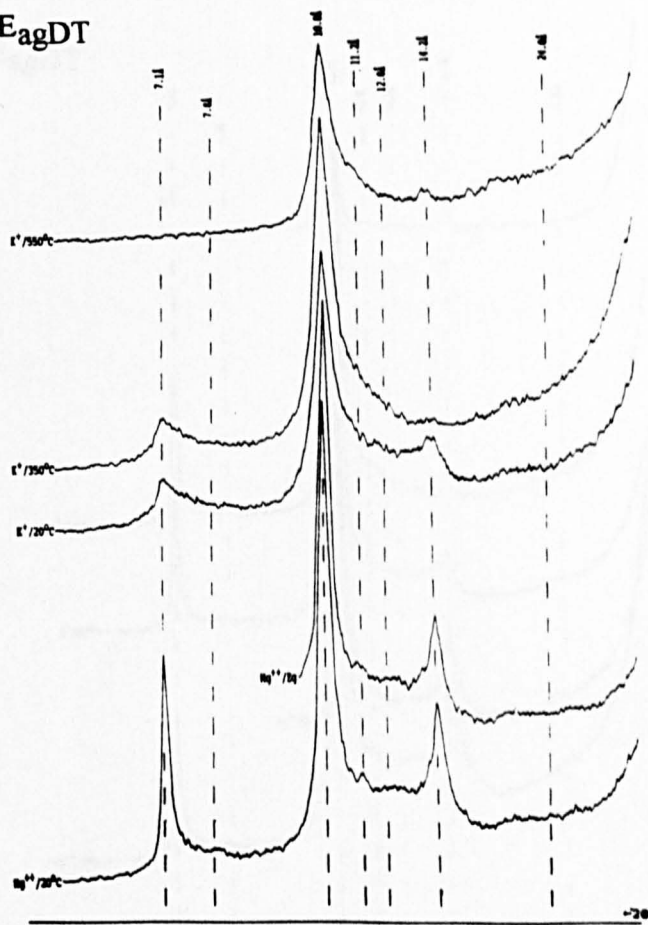


2. Samples treated with Mg^{++} and K^+ saturation

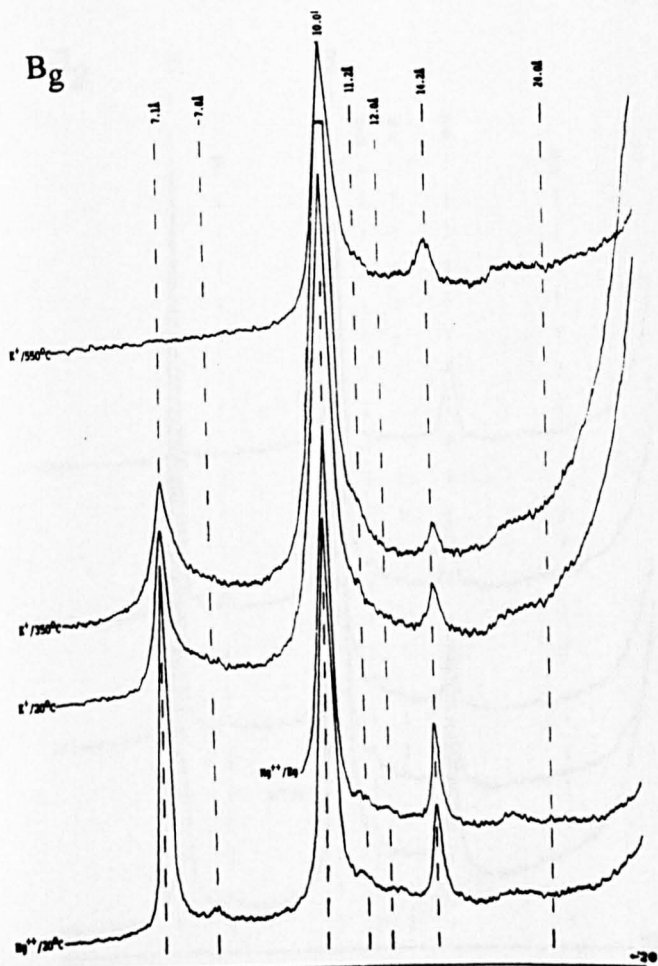
E_{ag}



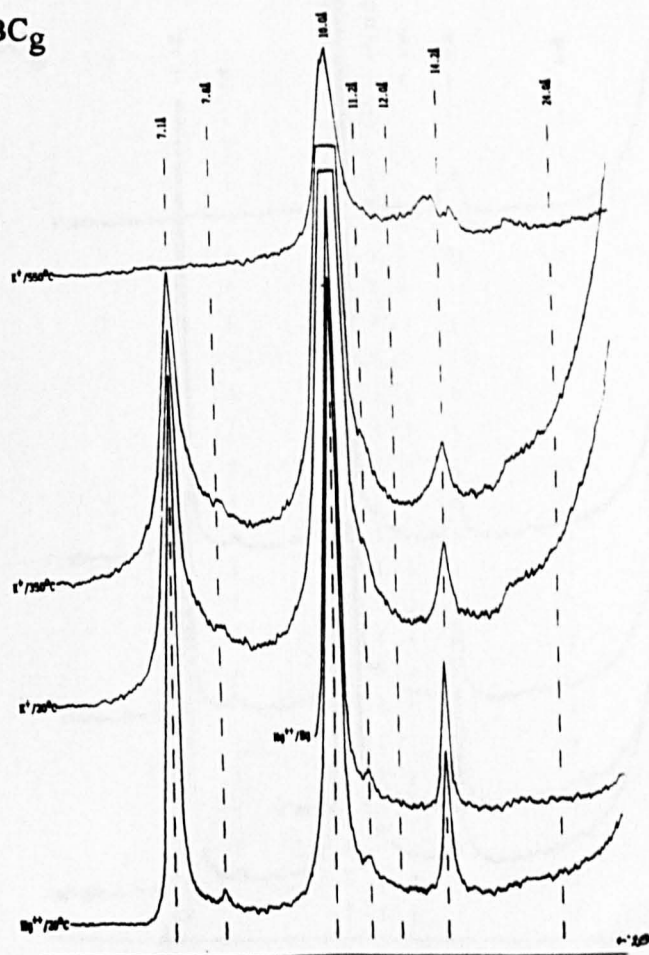
E_{agDT}



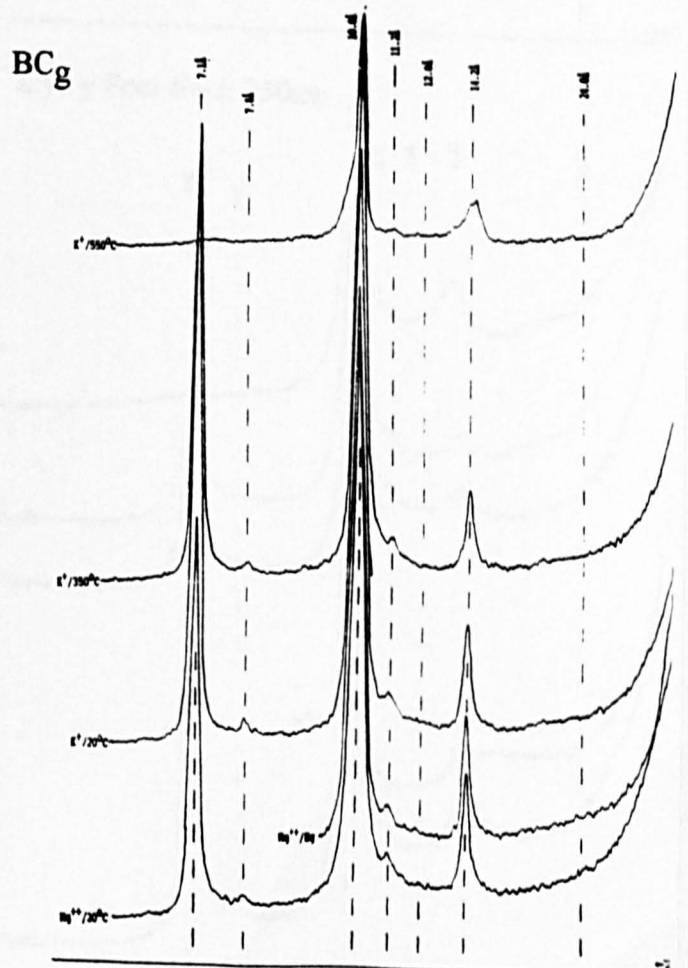
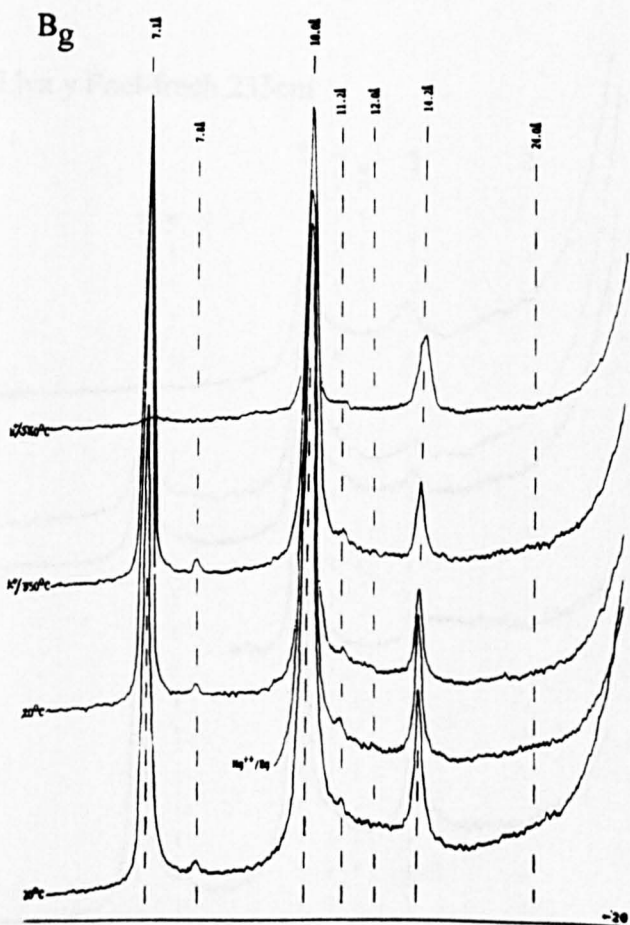
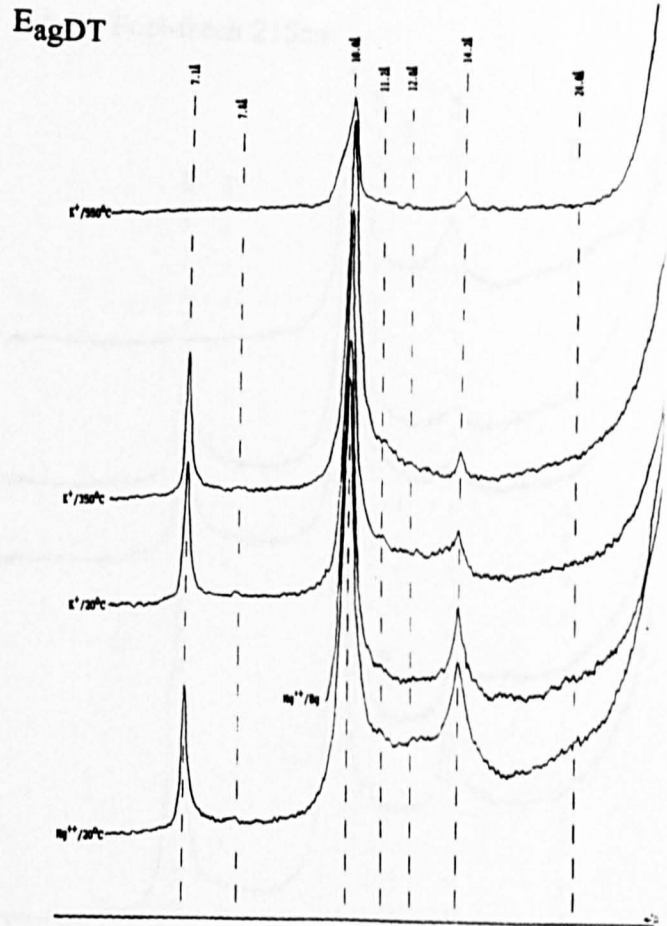
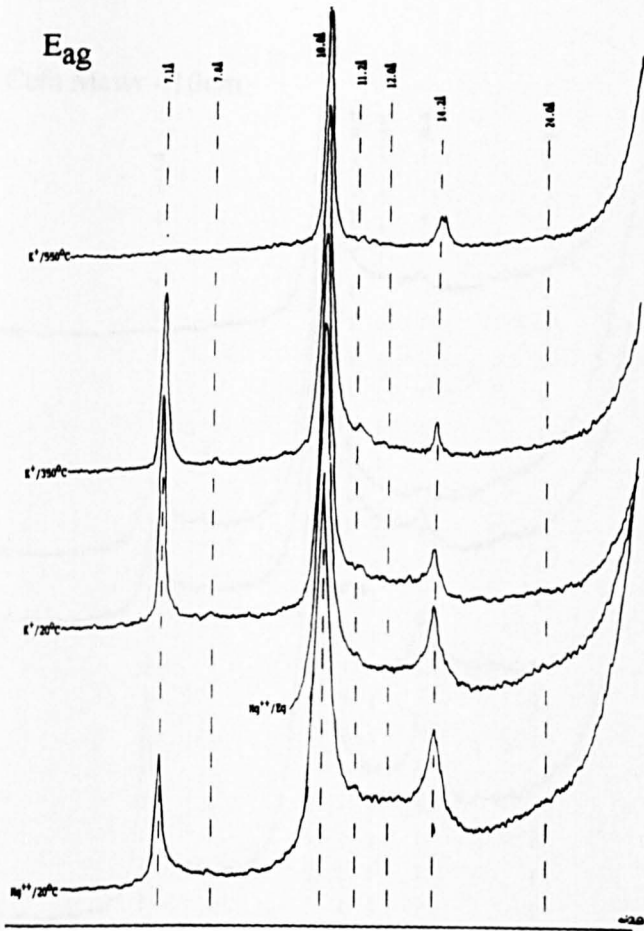
B_g



BC_g



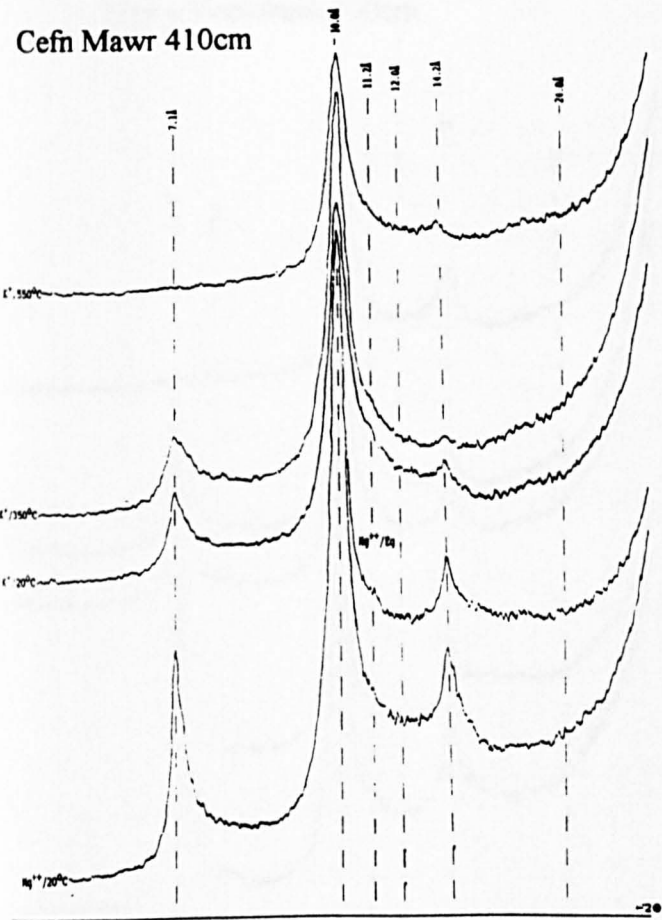
3. Samples cleaned with 0.5M NaOH and then saturated with Mg^{++} and K^+



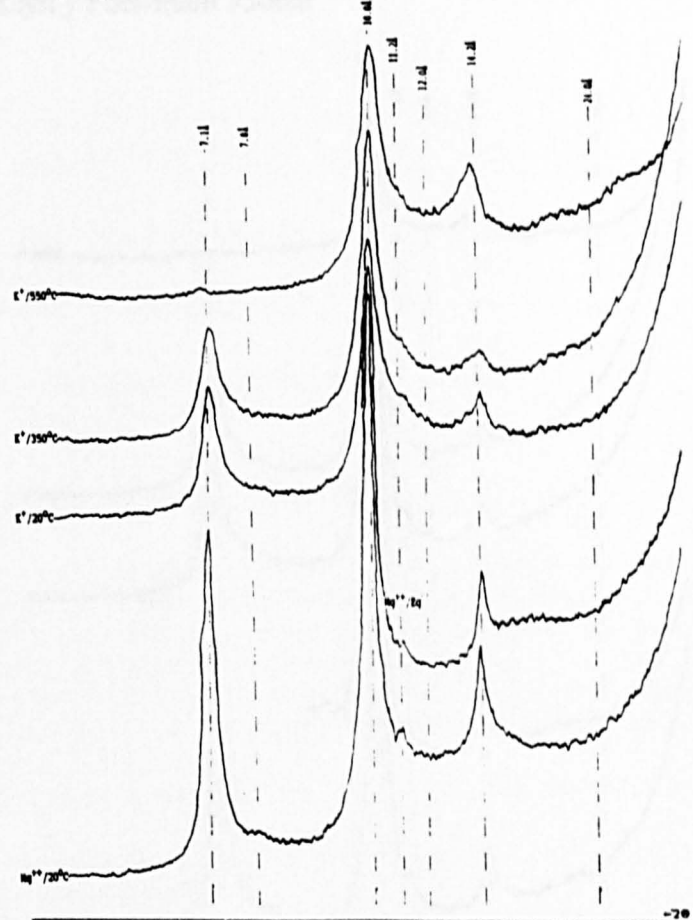
Appendix IIIf

XRD traces from the clay fraction form minerogenic core materials.

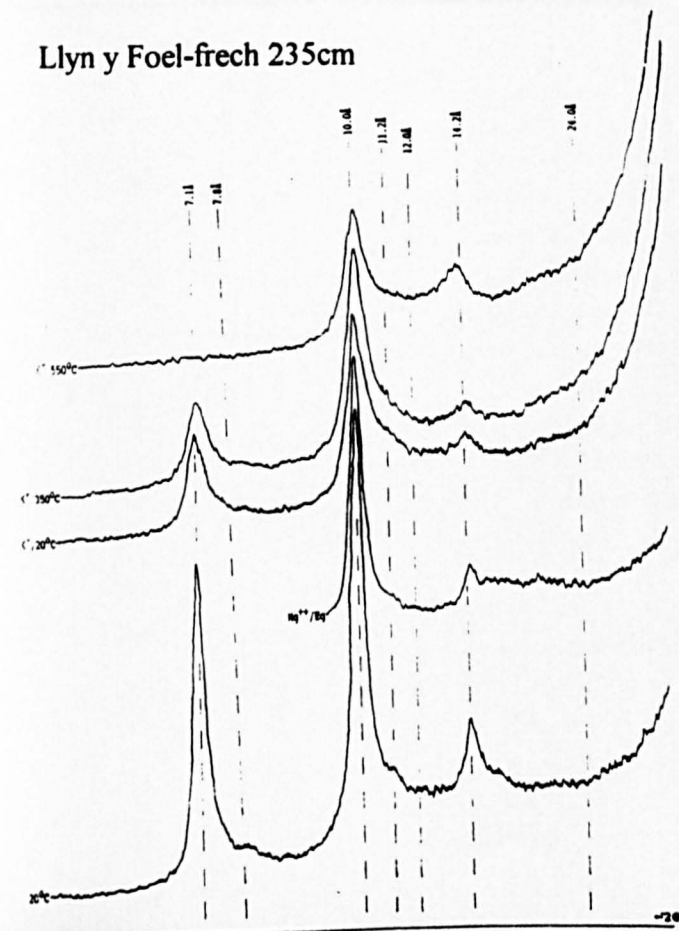
Cefn Mawr 410cm



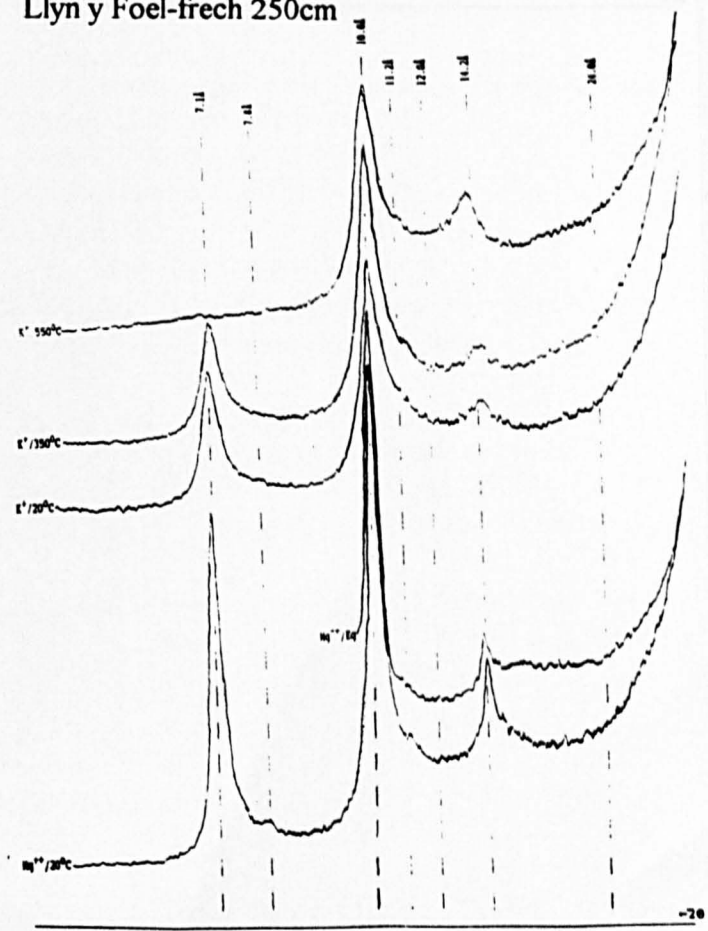
Llyn y Foel-frech 215cm



Llyn y Foel-frech 235cm

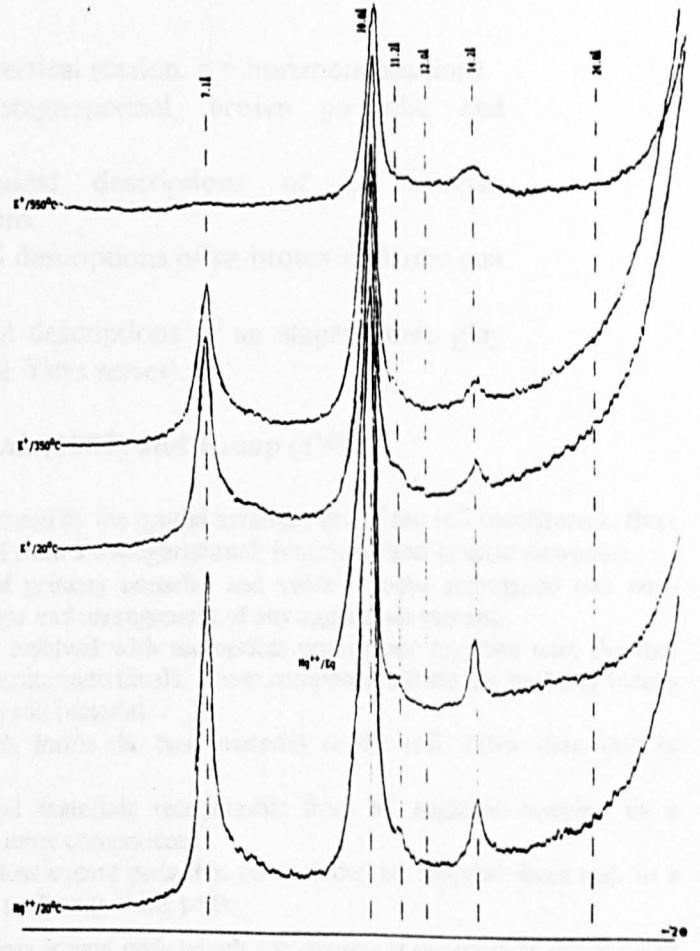
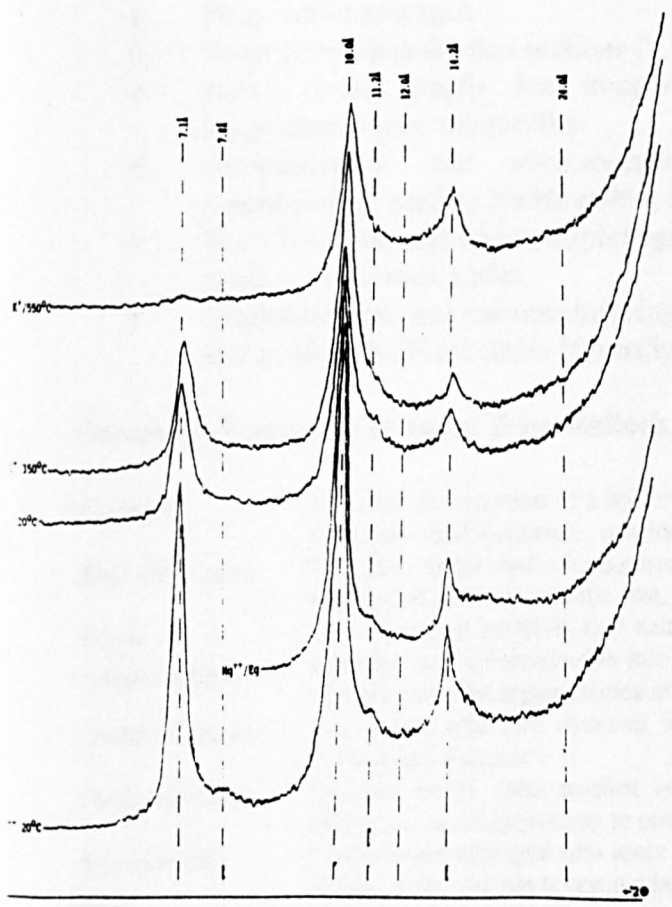


Llyn y Foel-frech 250cm



Llyn y Foel-frech 300cm

Llyn y Foel-frech 320cm



Appendix IV

Soil micromorphology

- a Point count averages.
- b Point count data for thin sections (v = vertical section; h = horizontal section).
- c Point count graphs for ironpan stagnopodzol, brown podzolic and stagnohumic gley soil profiles.
- d Morphological and micromorphological descriptions of an ironpan stagnopodzol profile, the Hiraethog series.
- e Morphological and micromorphological descriptions of an brown podzolic soil profile, the Manod series.
- f Morphological and micromorphological descriptions of an stagnohumic gley soil profile, the Freni series (formally the Ynys series).

Glossary of terms used, taken from Bullock *et al.* (1985) and Kemp (1985).

Fabric:	The total organisation of a soil, expressed by the spatial arrangement of the soil constituents, their shape, size and frequency, considered from a configurational, functional and genetic viewpoint.
Soil structure	The size, shape and arrangement of primary particles and voids in both aggregated and non-aggregated material and the size, shape and arrangement of any aggregates present.
Basic components	The individual particles that can be resolved with the optical microscope together with the fine material that is unresolvable into discrete individuals. These components form the building blocks of more complex organisations of the soil material.
Groundmass	The coarse and fine material which forms the base material of the soil, other than that in pedological features.
Pedofeatures	Discrete fabric units present in soil materials recognisable from an adjacent material by a difference in concentration in one or more components.
Spheroidal peds	Particles are arranged into more or less equant peds that are bounded by rounded faces and, as a consequence, are not accommodated to the adjoining peds.
Blocky peds	Particles are arranged into more or less equant peds which are <i>angular</i> if bounded by flat surfaces and <i>subangular</i> if bounded by flat and rounded surfaces.
Packing voids	Equant to elongate voids which occur between single mineral grains (<i>simple</i>), aggregates (<i>compound</i>) or between single grains and microaggregates (<i>complex</i>)
Vughs	Relatively large, irregular voids which cannot be considered as packing voids
Vesicles	Regular, smoothed voids which do not fit the criteria of any other types
Chambers	Spheroidal voids which are connected to channels
Channels	Voids which may be linear and are generally cylindrical in three dimensions
Planar voids	Planar in three dimensions but appear linear in thin section. Sharp changes in direction common.
Pellicular alteration	Alteration starting at the surface of a mineral and proceeding towards its centre.
b-fabric	"Birefringence fabric". Fabric of the fine mass between crossed polarisers can be described by the orientation and distribution of the patterns of interference colours and by their nature.
Hypo-coatings	Occur immediately adjoining rather than on the surface with which they are associated
Quasi-coatings	Related to the surfaces of voids, grains and aggregates but not immediately adjoining them.
Typic	Applies to all coatings when they are approximately regular in thickness throughout their length.
Textural pedofeatures	Pedofeatures consisting of accumulations of particles of any size and in variable proportions e.g. <i>cutan</i> (clay + silt), <i>argillans</i> (clay), <i>organans</i> (organic matter), <i>ferrans</i> (iron).

Appendix IVa

Point count averages

Sample	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo-mineral	Pedofeatures
Ironpan stagnopodzol								
P1 Oh	37.8	1.5	4.9	48.8	6.2	0.8	0.0	0.0
Eag	17.7	0.0	27.2	9.2	0.6	1.0	39.0	5.3
Bs1	13.8	48.0	16.8	1.5	0.4	14.6	0.0	4.9
Bs2	24.9	25.7	17.4	0.2	0.2	28.2	0.0	3.4
BC	13.1	19.8	12.7	0.4	0.2	53.5	0.0	0.3
P2 Oh	28.3	0.0	5.0	61.6	4.6	0.5	0.0	0.0
Eag	22.1	43.0	19.0	5.6	1.3	2.5	6.5	0.0
Bs1	12.7	35.6	21.2	0.3	0.4	27.8	0.0	0.0
Bs2	21.7	19.4	10.6	0.0	1.1	46.6	0.0	0.6
BC	13.2	31.5	26.1	0.0	0.0	29.0	0.0	0.2
P1 Oh	38.4	0.0	5.2	51.2	5.2	0.0	0.0	0.0
Eag	21.9	0.6	16.6	7.0	5.7	1.6	46.2	0.4
Bs1	18.4	42.0	22.3	0.3	0.8	9.2	0.0	7.0
Bs2	30.4	26.0	13.4	0.6	0.0	28.0	0.0	1.6
BC	14.7	25.7	15.4	0.2	0.0	43.8	0.0	0.2
Brown podzolic soil								
P1 Ah	37.8	0.0	0.0	2.8	4.0	3.0	52.0	0.4
Bs1	25.4	33.8	16.6	0.4	1.2	22.0	0.0	0.6
Bs2	16.2	28.4	12.2	0.2	0.2	42.3	0.0	0.5
BC	12.9	35.4	27.9	0.4	0.4	22.2	0.0	0.8
Stagnohumic gley soil								
P1 Oh	32.4	0.0	8.6	49.0	7.0	3.0	0.0	0.0
Eag	20.4	0.0	14.4	12.6	4.3	2.7	45.6	0.0
Bg	10.2	39.6	37.0	1.6	1.0	7.4	2.0	1.2
BCg	4.0	52.4	32.4	0.8	0.0	9.5	0.0	0.9
P2 Oh	29.7	0.0	9.5	54.3	6.5	0.0	0.0	0.0
Eag	16.0	0.0	13.9	14.7	3.8	2.0	49.6	0.0
Bg	10.2	43.6	26.1	0.6	1.8	9.3	0.0	8.4
BCg	4.0	35.8	20.8	0.5	0.3	33.8	0.0	4.8

Appendix IVb - Point count data for thin sections

Ironpan stagnopodsolic profiles

Profile 1.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Oh(h)	42.6	2.1	3.4	46.3	5.6	0.0	0.0	0.0	0.0	0.0	0.0
Oh(v)	33.0	0.9	6.4	51.2	6.7	1.8	0.0	0.0	0.0	0.0	0.0
Eag(h)	24.7	0.0	24.3	8.8	1.1	0.8	40.3	0.0	0.0	0.0	0.0
Eag(v)	10.7	0.0	30.1	9.7	0.1	1.1	37.7	0.0	0.0	0.0	10.6
Bs1(h)	13.2	47.0	17.3	1.0	0.6	16.8	0.0	0.0	0.0	0.0	4.1
Bs1(v)	14.5	49.1	16.4	1.9	0.2	12.3	0.0	0.0	0.0	0.0	5.6
Bs2(h)	35.0	29.6	20.8	0.3	0.4	11.1	0.0	0.8	0.0	0.0	2.8
Bs2(v)	14.9	21.8	14.1	0.0	0.0	46.1	0.0	0.0	0.0	0.0	3.1
BC(h)	10.8	21.5	14.7	0.5	0.1	52.1	0.0	0.0	0.2	0.0	0.1
BC(v)	15.4	18.1	10.7	0.3	0.4	55.0	0.0	0.0	0.1	0.0	0.0

Profile 2.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Oh(h)	30.2	0.0	5.4	61.5	2.9	0.0	0.0	0.0	0.0	0.0	0.0
Oh(v)	26.4	0.0	4.7	61.8	6.4	0.7	0.0	0.0	0.0	0.0	0.0
Eag(h)	23.5	43.0	20.7	0.9	0.4	2.1	9.3	0.0	0.0	0.1	0.0
Eag(v)	20.7	43.1	17.2	10.2	2.2	2.9	3.5	0.0	0.0	0.0	0.0
Bs1(h)	12.5	38.5	22.0	0.6	0.3	23.6	2.5	0.0	0.0	0.0	0.0
Bs1(v)	12.9	32.6	20.4	0.0	0.4	32.1	1.6	0.0	0.0	0.0	0.0
Bs2(h)	18.7	18.7	6.5	0.0	1.2	54.2	0.0	0.0	0.0	0.0	0.7
Bs2(v)	24.7	20.1	14.7	0.0	1.0	38.9	0.0	0.0	0.0	0.0	0.6
BC(h)	12.4	32.2	21.5	0.0	0.0	33.8	0.0	0.0	0.0	0.1	0.0
BC(v)	13.9	31.0	30.7	0.0	0.0	24.1	0.0	0.3	0.0	0.0	0.0

Profile 3.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Oh(h)	38.9	0.0	4.9	49.6	6.6	0.0	0.0	0.0	0.0	0.0	0.0
Oh(v)	38.0	0.0	5.4	52.9	3.7	0.8	0.0	0.0	0.0	0.0	0.0
Eag(h)	24.6	0.0	17.2	6.2	10.9	1.9	39.2	0.0	0.0	0.0	0.0
Eag(v)	19.2	0.7	15.7	7.7	0.5	2.3	53.0	0.0	0.0	0.0	0.9
Bs1(h)	19.7	34.0	23.8	0.1	0.7	16.0	0.0	0.0	0.0	0.0	5.7
Bs1(v)	17.2	50.1	20.8	0.4	0.8	2.4	0.0	0.0	0.0	0.0	8.3
Bs2(h)	24.1	30.3	11.0	0.0	0.0	33.0	0.0	0.0	0.0	0.0	1.6
Bs2(v)	36.7	22.1	16.2	1.3	0.1	22.1	0.0	0.0	0.0	0.0	1.5
BC(h)	16.0	17.5	12.5	0.1	0.0	53.9	0.0	0.0	0.0	0.0	0.0
BC(v)	13.4	33.9	18.3	0.2	0.1	33.6	0.0	0.0	0.0	0.0	0.5

Typical podzolised brown earth.

Profile 1.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Ah(h)	43.6	0.0	0.8	2.8	2.8	1.5	49.3	0.0	0.0	0.0	0.0
Ah(v)	32.0	0.0	0.0	2.9	5.1	4.6	54.7	0.0	0.0	0.0	0.7
Bs1(h)	28.6	31.7	16.1	0.0	0.0	23.0	0.0	0.0	0.0	0.0	0.6
Bs1(v)	22.1	35.9	17.2	0.8	2.5	21.0	0.0	0.0	0.0	0.0	0.5
Bs2(h)	19.5	26.3	10.1	0.0	0.2	43.4	0.0	0.0	0.0	0.0	0.5
Bs2(v)	12.8	30.4	14.4	0.4	0.3	41.2	0.0	0.0	0.0	0.0	0.5
BC(h)	15.0	40.6	32.5	0.2	0.2	10.3	0.0	0.2	0.1	0.3	0.2
BC(v)	10.8	30.1	23.1	0.4	0.4	34.1	0.0	0.4	0.0	0.1	0.3

Stagnohumic gley soil.

Profile 1.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Oh(h)	33.9	0.0	7.5	47.2	6.1	5.3	0.0	0.0	0.0	0.0	0.0
Oh(v)	30.9	0.0	9.6	51.1	7.8	0.6	0.0	0.0	0.0	0.0	0.0
Eag(h)	17.4	0.0	16.8	14.9	4.7	3.2	43.0	0.0	0.0	0.0	0.0
Eag(v)	23.3	0.0	11.9	10.2	3.9	2.2	48.5	0.0	0.0	0.0	0.0
Bg(h)	11.4	37.3	36.6	1.4	2.0	9.5	0.0	0.3	0.0	0.0	1.5
Bg(v)	9.1	42.2	38.0	0.9	0.0	5.2	4.0	0.0	0.0	0.0	0.5
BCg(h)	6.3	56.3	29.2	0.9	0.0	6.5	0.0	0.4	0.6	0.0	0.0
BCg(v)	1.8	48.6	35.7	0.7	0.0	12.5	0.0	0.1	0.1	0.0	0.5

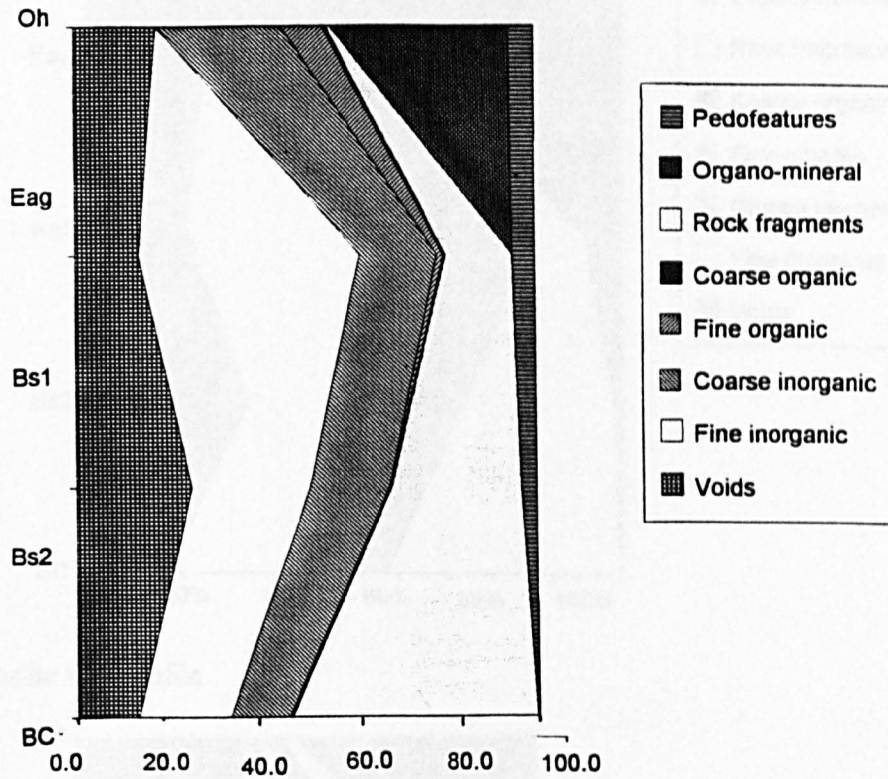
Profile 2.

	Voids	Inorganic fine	Inorganic coarse	Organic fine	Organic coarse	Rock fragments	Organo- mineral	Argillans	Siltans	Cutans c + z	Amorph. + crypt.
Oh(h)	30.6	0.0	9.6	54.5	5.1	0.0	0.0	0.0	0.0	0.0	0.0
Oh(v)	28.7	0.0	9.3	53.9	7.8	0.1	0.0	0.0	0.0	0.0	0.0
Eag(h)	15.1	0.0	17.0	15.3	5.1	0.4	47.1	0.0	0.0	0.0	0.0
Eag(v)	16.9	0.0	10.8	14.1	2.6	3.5	52.1	0.0	0.0	0.0	0.0
Bg(h)	8.0	46.5	26.5	0.3	1.7	8.3	0.0	0.0	0.0	0.1	8.6
Bg(v)	12.5	40.7	25.7	1.0	1.9	10.3	0.0	0.1	0.0	1.3	6.5
BCg(h)	4.7	30.1	19.5	0.6	0.6	38.1	0.0	0.1	0.0	1.4	4.9
BCg(v)	3.3	41.6	22.0	0.4	0.0	29.4	0.0	0.1	0.0	1.4	1.8

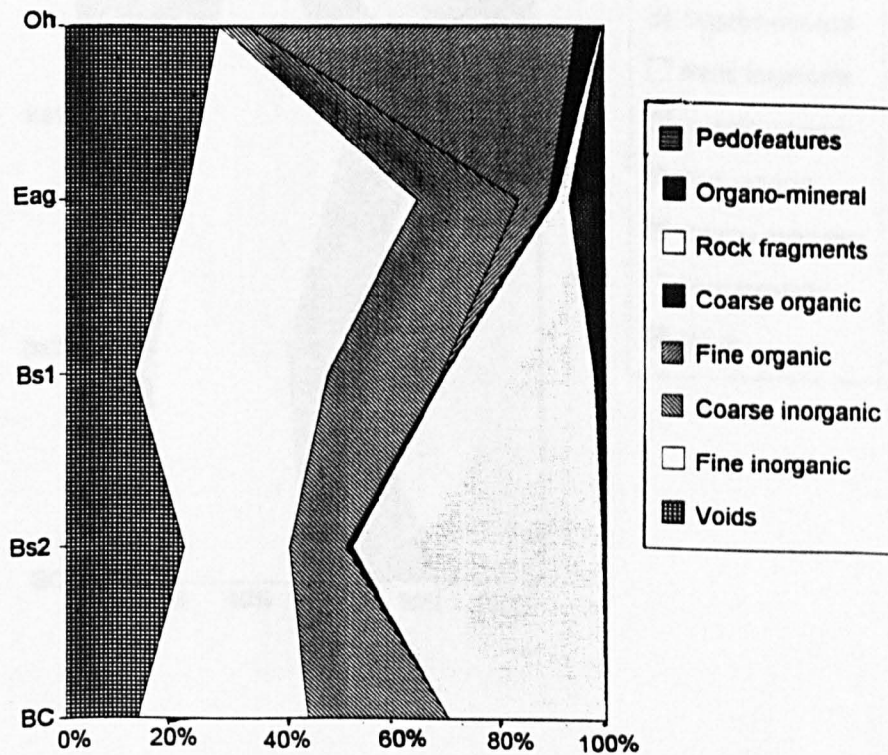
Appendix IVc

Point count data for ironpan stagnopodzol, brown podzolic and stagnohumic gley soil profiles.

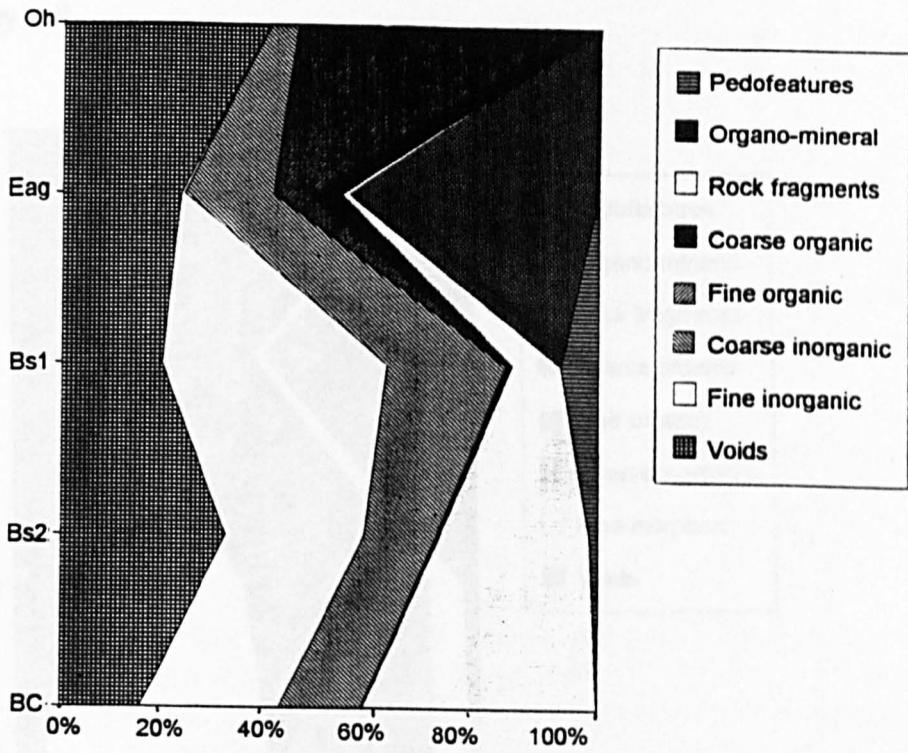
Ironpan stagnopodzolic profiles
Profile 1



Profile 2

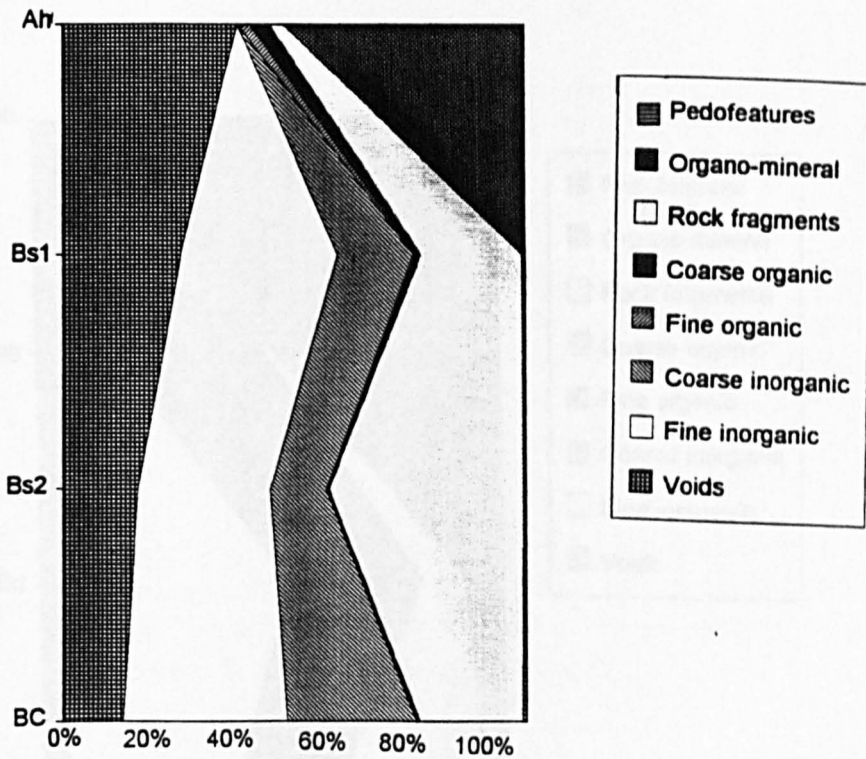


Profile 3

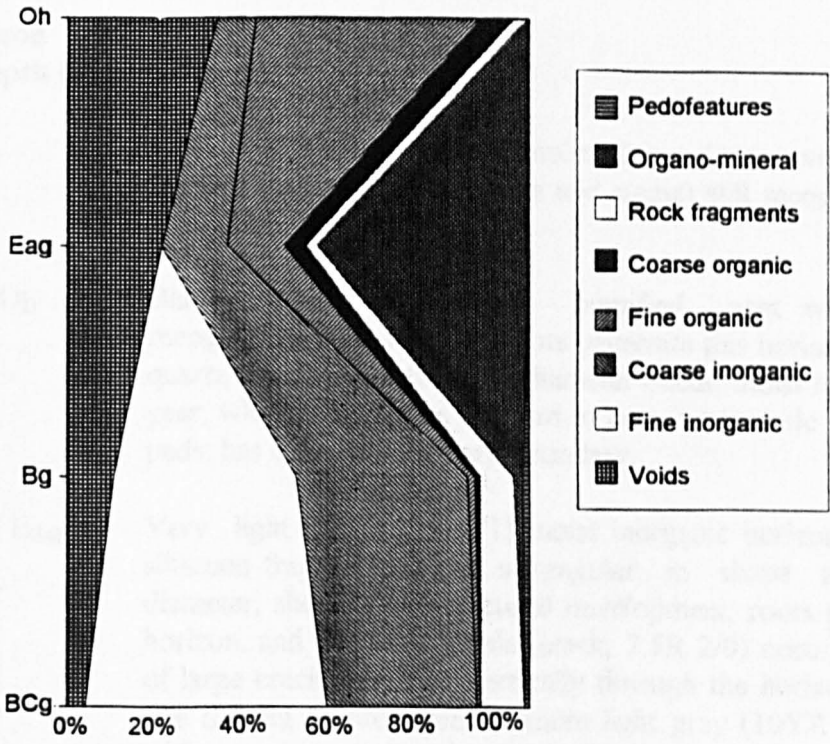


Brown podzolic soil profile

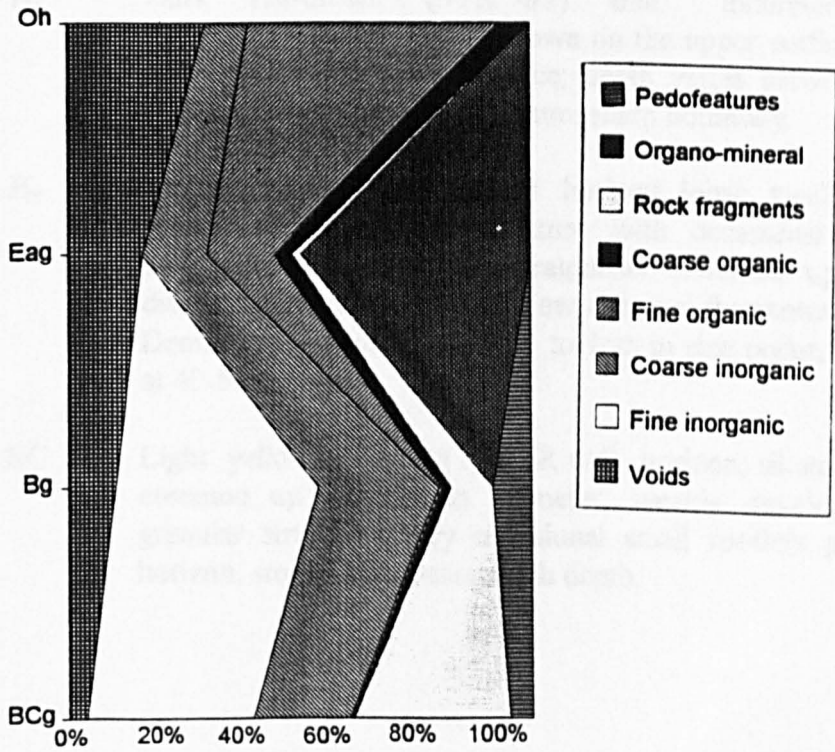
b) Profile 1



Stagnohumic gley soil
Profile 1



Profile 2



Appendix IVd Morphological and micromorphological description of an ironpan stagnopodzol profile, the Hiraethog Series,

Horizon & depth (cm)	Description
0-5 L	Brown (7.5YR 5/4) fresh, moist litter layer with many plant remains (grass and moss roots and stems) still recognisable; loose with an abrupt boundary.
5-14 O _h	Black (7.5YR 2/0) well humified peat with very few recognisable plant remains; roots penetrate this horizon; occasional quartz grains up to 0.5cm in diameter occur; moist for most of the year; when dry it forms medium to coarse prismatic and columnar peds; has an abrupt to sharp boundary.
14-24 E _{ag}	Very light grey (5Y 7/1) moist inorganic horizon; quartz and siltstone fragments occur, subangular in shape up to 1cm in diameter; shows little structural development; roots penetrate this horizon, and humic materials (black, 7.5R 2/0) occur on the faces of large cracks running vertically through the horizon. Few very fine distinct to prominent medium light grey (10YR 7/2) mottles with sharp boundaries; sharp boundary
24-25 B _f	Dark red-brown (5YR 4/3) thin indurated continuous undulating horizon, darker brown on the upper surface; root mat often present on upper surface; depth varies between 42-50cm, thickness varies between 5-10mm; sharp boundary.
25-51 B _s	Reddish yellow (7.5YR 6/6) horizon; loose, weakly developed granular (fine-medium) structure with occasional small roots penetrating; angular siltstone fragments common, up to 1cm in diameter. Gradual boundary. Few charcoal fragments of <i>Alnus</i> (P. Denne, pers. comm., 1995) up to 1cm in size occur, concentrated at 40-50cm depth.
51-90 BC	Light yellowish brown (10YR 6/4) horizon; siltstone fragments common up to 6cm in diameter; weakly developed medium granular structure; very occasional small rootlets penetrate the horizon; stoniness increases with depth.

O_h (Vertical section)

Microstructure

Pedality strongly developed. Peds: (a) ultrafine to very fine subangular blocky peds; unaccommodated surfaces: (b) ultrafine spheroidal crumb peds (<5% total ped area); random distribution.

Porosity is $\approx 30\%$. Inter-aggregate voids dominate: compound packing voids; rough unaccommodating walls; up to 1mm in diameter. Intra-aggregate voids; coarse micro vughs with undulating unaccommodating surfaces; all have a random distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 30:70

Silurian siltstone fragments: up to 1200 μ m; oblate to prolate rough to undulating subangular; total <2%; random distribution. Single mineral grains: total $\approx 5\%$; up to 100 μ m; largest dominated by oblate to equant smooth subrounded quartz grains; occasional chlorite grains, mica fragments and rare tourmaline grains; coarse fraction has a random distribution.

Fine fraction totals $\approx 3\%$ as dense incomplete void infillings of pale grey fine silts and clays; included large fragments; little interference colour; speckled limpidity.

Basic Organic Component c/f ratio 15:85

Coarse fraction as (a) organ residues: up to 1500 μ m; pale yellow-brown (PPL); bright interference colours; always associated with voids; or black residues, 500 μ m; isotropic; (b) tissue residues: up to 300 μ m; black (PPL). All the coarse fraction has a random distribution.

Fine organics as (a) black; 100 μ m; often embedded in soil matrix; (b) red-brown dense incomplete void infilling; usually isotropic; can occur as thin ($\approx 40\mu$ m) strands within voids giving yellow orange interference colours; (c) pale brown isotropic material as the matrix; (d) rare pollen grains (*Betula*) embedded in the matrix; (e) yellow (PPL) dense complete void infillings with aggregate extinction.

Groundmass

Organic, pale brown (PPL); isotropic; occasional small (<40 μ m) birefringent areas with white/grey interference colours.

Pedofeatures

None

O_h (Horizontal Section)

Microstructure

Pedality moderately to strongly developed; peds dominated by ultrafine to very fine subangular blocky peds; ultrafine spheroidal crumb peds also occur; rough unaccommodated surfaces; random distribution.

Porosity is 30-40%. Inter-aggregate voids as compound packing voids; rough unaccommodated surfaces; up to 1mm in width; extend for several mm's. Intra-aggregate voids as coarse micro vughs; undulating unaccommodated surfaces; random distribution.

Basic Mineral Component c/f_{10μm} c/f ratio 80:20

Silurian siltstone fragments: total <1%; up to 200μm; oblate, undulating sub-rounded; random distribution. Single mineral grains; up to 100μm; oblate to equant undulating sub- rounded quartz fragments; random distribution; occasional mica flakes and chlorite grains.

Fine fraction: inorganic; recognisable only as small (<10μm) birefringent areas within the organic groundmass.

Basic Organic Components c/f ratio 10:90

Coarse fraction totals <5% as (a)organ residues: interference always occur in voids; random distribution; or as black structures; (b)tissue residues: black; embedded in the soil matrix; up to 400μm.

Fine fraction dominated by pale brown, isotropic amorphous groundmass; also as (a) pale yellow laminated; orange-yellow interference colours; (b)black fragments embedded in the matrix, (c) red-brown isotropic incomplete void infillings.

Groundmass

Inorganic; occasional inclusions of inorganic silts and fine sands; brown in PPL; isotropic.

Pedofeatures

None

Eag (Vertical section)

Microstructure

Pedality moderately developed; peds as (a)ultrafine subangular blocky peds; rough unaccommodated surfaces; (b)ultrafine spheroidal granular peds; occur in groups in void spaces; undulating unaccommodated surfaces; random distribution.

Porosity is 10-20%. Inter-aggregate voids: complex packing voids with rough unaccommodated surfaces; compound packing voids and coarse-meso to fine-macro vughs with undulating unaccommodated surfaces where lower organic matter levels. Intra-aggregate voids as fine to medium meso-vughs; undulating unaccommodated surfaces; random distribution.

Basic Mineral Component c/f_{10μm} c/f ratio

Silurian siltstone fragments: total <2%; up to 2mm; oblate to equant undulating subrounded; occasionally exhibit thick pellicular alteration; random distribution; some fragments show complete alteration (cryptic). Single mineral grains: up to 100μm; largest are oblate to equant smooth subangular quartz grains; occasionally exhibit polycrystallinity or undulose extinction; remainder composed of quartz grains, feldspars, mica flakes and heavy minerals (chlorite with occasional tourmaline).

Fine fraction: fine silts and clays stained brown; dark interference colours; speckled limpidity; frequent inclusions exhibiting UV fluorescence.

Basic Organic Component c/f ratio

Coarse fraction as (a)organ residues: yellow brown; bright interference colours; up to 1000μm; always occur in voids; (b)tissue residues rare: up to 200μm; black; random distribution; (c)occasional pollen grains, typically tricolporate, yellow, isotropic and exhibit UV fluorescence; some shell-like structures up to 40μm and exhibiting UV fluorescence.

Fine fraction as (a) brown pigmentation of matrix, varying in extent across the horizon; (b)yellow isotropic dense incomplete void infillings; (c)brown-red isotropic typical void coatings up to 400μm thick; often broken and disjointed.

Groundmass

Organo-mineral, extent of organic pigmentation varies; pale to dark brown (PPL); stipple-speckled b-fabric; gives an overall porphyric related distribution pattern.

Pedofeatures

Amorphous and cryptocrystalline pedofeatures as (a)see organic fine material; (b)typic weakly impregnated nodules; 1mm in diameter; red-brown (PPL); red-orange birefringence colours; associated with fine red-brown isotropic organics; (c)excrement pedofeatures as mammilated excrements; up to 50μm in diameter; organo-mineral; clustered basic distribution; show signs of aging (coalescence into very porous to porous deposits).

Eag (Horizontal section)

Microstructure

Pedality weakly to moderately developed; more well developed where higher levels of organic matter impregnation; peds total $\approx 80\%$; (a) ultrafine to very fine subangular blocky peds; rough to undulating unaccommodated surfaces; (b) ultrafine spheroidal crumb peds; usually concentrated within voids; associated with areas of higher organic matter.

Porosity is $\approx 20\%$. Inter-aggregate voids: (a) complex packing voids; rough unaccommodated surfaces; (b) fine meso to fine macro vughs; undulating unaccommodated surfaces; become more dominant in areas of lower organic matter. Intra-aggregate voids as fine to medium meso vughs; undulating unaccommodated surfaces; basic distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio

Silurian siltstone fragments: up to 800 μ m; total <10% of coarse fraction; oblate smooth subrounded; random distribution; some fragments show complete alteration. Single mineral grains; up to 400 μ m; largest dominated by subangular to angular smooth quartz grains; occasionally polycrystalline or exhibit undulose extinction; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with rare tourmaline and rutile).

Fine fraction: organo-mineral; extent of pigmentation varying; pale grey to dark brown (PPL); grey to dark interference colours; dotted limpidity; small shell-like, often deformed structures exhibits UV fluorescence.

Basic Organic Component c/f ratio

Coarse fraction: (a) tissue residues; up to 1mm; dark-brown (isotropic)/black (PPL); random distribution; (b) organ residues; yellow-brown in (PPL); bright interference colours; always associated with voids; (c) pollen grain (tricolporate); yellow; isotropic; random.

Organic fine material: (a) red-brown isotropic dense incomplete void infillings; (b) pale-yellow isotropic incomplete/complete void infillings.

Groundmass

Organo-mineral to varying degrees; stipple-speckled b- fabric; gives an overall porphyric related distribution.

Pedofeatures

(a) Amorphous and cryptocrystalline pedofeatures; see organic fine material

(B) Excrement pedofeatures: mammillated excrements up to 50 μ m in diameter; organo-mineral; clustered basic distribution; show signs of aging (coalescence into porous to very porous deposits).

Bf (Vertical section)

Microstructure

Very weakly developed pedality. Ultrafine to very fine subangular to angular blocks; rough to undulating partially accommodated surfaces; random distribution.

Porosity is <5%. Inter-aggregate voids: up to 600µm in diameter as (a) planar voids; undulating accommodated surfaces; straight crack pattern; random distribution; (b) coarse meso to fine macro vughs; rough to undulating surfaces; sometimes parallel referred distribution pattern (to the upper surface of the pan).

Basic Mineral Component c/f_{10µm} c/f ratio 30:70

Silurian siltstone fragments: oblate, smooth subangular; exhibit pellicular to thick pellicular alteration; up to 4mm; random distribution. Single mineral grains; up to 800µm; largest dominated by equant to oblate smooth subrounded quartz grains; occasionally exhibit undulose extinction; remainder composed of quartz grains, feldspars and occasional chlorite grains.

Fine fraction composed of fine silts and clays; totally stained red-brown (PPL); red-brown to orange birefringence.

Basic Organic Components c/f ratio 40:60

Coarse fraction as organ residues; parallel referred distribution (along upper surface of iron pan); up to 500µm pale yellow brown (PPL); bright interference colours; occasionally deformed away from circular shape by the upper surface of the pan.

Fine fraction as red-orange deposits; up to 700µm thick; isotropic dense complete void infillings; dense incomplete void infillings; typical void coatings; inclusions of silt and fine sand sized grains but are otherwise pure; some organic matter as organic pigmentation of the mineral material.

Groundmass

Organo-mineral; red/orange brown (PPL); stipple-speckled b- fabric where visible.

Pedofeatures

(a) See organic fine material and excretion pedofeatures (within voids).

(b) Amorphous and cryptocrystalline pedofeatures as typical, strongly impregnated nodules; up to 700µm in diameter; dark red (PPL); dark red interference colours; good contrast; also general staining of the groundmass.

B₃1 (Vertical section)

Microstructure

Pedality moderately developed. Peds as ultrafine to very fine subangular blocks; undulating to rough partially accommodated to unaccommodated surfaces; random distribution

Porosity is 20%. Inter aggregate voids as complex packing voids; undulating to rough partially accommodated walls; up to 2cm long; random distribution; towards top of horizon grade into medium-meso to fine-macro vesicles; smooth unaccommodated walls.

Basic Mineral Component c/f₁₀μm c/f ratio 50:50

Silurian siltstone fragments: up to 1cm; oblate to prolate smooth rounded to subrounded; occasionally show pellicular alteration; total ≈20-30%; random distribution; increase in % with depth. Single mineral grains: up to 200μm; total ≈20%; largest composed of oblate undulating subangular quartz grains; occasionally exhibit polycrystallinity or undulose extinction; remainder composed of quartz grains, mica flakes, amphiboles and heavy minerals (chlorite with rare rutile and tourmaline).

Fine fraction inorganic; red-brown coloured (PPL); dark grey interference colours; dotted limpidity.

Basic Organic Component c/f ratio 30:70

Coarse fraction totals <1% as organ residues; yellow-brown (PPL); bright interference colours.

Fine fraction totals <1% as (a)black; embedded in the matrix; (b)orange-red, isotropic, dense incomplete void infilling; usually associated with typic hypo-coatings; red-orange interference colours.

Groundmass

Inorganic; red-brown to grey (PPL); lighter higher up the horizon; white/grey interference colours; stipple-speckled b- fabric; gives overall porphyric related distribution pattern.

Pedofeatures

Total ≈10%. Amorphous and cryptocrystalline pedofeatures; (a)nodules more common towards the top of the horizon; red-brown (PPL); red-orange birefringence; range in size (100 to 1500μm); typic; occasionally amiboidal; sometimes with halo's; pure to strongly impregnated; lower down the profile less common as soil becomes more generally red-brown coloured.

(b) See organic fine material.

B₅₁ (Horizontal section)

Microstructure

Pedality moderately developed; ultrafine to very fine subangular blocky peds; rough to undulating partially accommodated surfaces; comprise ≈85%; random distribution.

Porosity is ≈15%. Inter-aggregate voids as (a) complex packing voids; up to 3mm in diameter; run for several cm's; (b)medium-meso vesicles; (c)medium-meso chambers; random distribution.

Basic Mineral Component c/f_{10μm} c/f ratio 50:50

Silurian siltstone fragments: up to 1cm; oblate to equant undulating rounded; occasional planar voids through them with undulating accommodated surfaces; random distribution. Single mineral grains total ~20%; up to 200μm; largest dominated by oblate to equant subrounded undulating quartz grains; occasionally exhibiting polycrystallinity or undulose extinction; random distribution; remainder composed of quartz grains, feldspars, mica flakes and heavy minerals (chlorite with rare zircon and tourmaline).

Fine fraction: inorganic; red-brown (PPL); dark-grey interference colours; does not exhibit UV fluorescence; dotted limpidity.

Basic Organic Component c/f ratio 50:50

Coarse fraction composed of (a)organ residues as yellow- brown structures; always occur in voids; bright birefringence; total <0.5%; (b)tissue residues, black deposits often embedded in the soil matrix.

Organic fine fraction totals <0.5%; dark red-brown to bright red isotropic deposits, often as typic void coatings.

Groundmass

Inorganic; red-brown (PPL); white-grey interference colours; stipple-speckled fabric giving an overall porphyric related distribution

Pedofeatures

Total ≈5%. Dominated by amorphous and cryptocrystalline pedofeatures as typic to amiboidal strongly to moderately impregnated nodules; range from 100-1000μm in diameter; red-brown (PPL); red-orange interference colours; occasionally remaining dark red-brown in XPL.

B_{s2} (Vertical section)

Microstructure

Moderately developed pedality. Peds dominated by ultrafine to very fine subangular blocks; rough to undulating partially accommodating walls; random distribution.

Porosity is $\approx 30\%$. (a) Inter-aggregate voids (up to 5mm in diameter); complex packing voids; occasionally tending towards chambers with interconnecting channels; undulating to rough partially accommodated walls; (b) Intra-aggregate voids dominated by medium-micro vughs; undulating unaccommodated walls; all have a random distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 70:30

Silurian siltstone fragments: total 60%; up to 4cm; oblate to equant smooth subangular; occasionally cracked or showing signs of pellicular alteration; random distribution. Single mineral grains; up to 80 μ m; largest dominantly oblate smooth subangular to angular quartz grains; occasionally exhibit undulose extinction; remainder composed of quartz grains, plagioclase feldspars, mica fragments and heavy minerals (chlorite with rare zircon, tourmaline and rutile).

The fine fraction is inorganic; red-brown (PPL); little birefringence; dotted limpidity; does not exhibit UV fluorescence.

Basic Organic Component c/f ratio 10:90

Organic matter totals <1%; dominated by the fine fraction as; (a) black; embedded within the matrix (b) dark red-brown; isotropic; typic void coatings rarely more than 20 μ m thick.

Coarse organic matter as organ residues; pale yellow (PPL); circular; bright interference colours; exhibit weak UV fluorescence; up to 120 μ m in diameter; always associated with voids.

Groundmass

Inorganic; fine silts and clays; red-brown (PPL); little birefringence; stipple-speckled b-fabric where visible; giving an overall porphyric related distribution pattern; does not exhibit UV fluorescence.

Pedofeatures

Total $\approx 3\%$. Dominated by amorphous and cryptocrystalline pedofeatures as; (a) typic occasionally amiboidal strongly to moderately impregnated nodules; dark red-brown (PPL); orange-red birefringence; (b) pure accumulations; bright red (PPL); bright orange birefringence and exhibiting extinction characteristics; no visible inorganic particles.

Textural pedofeatures are pale yellow, birefringent typic coatings up to 20 μ m thick.

B_s2 (Horizontal Section)

Microstructure

Pedality moderately to strongly developed. Peds as; (a) ultrafine to very fine sub-angular to angular blocks; undulating to rough partially accommodated surfaces; random distribution; (b) ultrafine spheroidal crumb peds; clustered basic distribution.

Porosity is $\approx 25\%$. (a) complex packing voids; up to 3mm in diameter; run for several cm's; zig-zag crack pattern; partially accommodated walls; random distribution; (b) fine meso-vesicles also occur; smooth unaccommodated surfaces; random distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 65:35

Silurian siltstone fragments: up to 3cm; equant to oblate smooth subrounded to subangular; random distribution; occasionally have planar voids running through them; undulating fully accommodated walls; or exhibit alteration. Single mineral grains: up to 100 μ m; largest dominated by oblate to equant smooth angular to subangular quartz grains; occasionally exhibit polycrystallinity or undulose extinction; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with rare of rutile and tourmaline).

Fine fraction is inorganic; red-brown (PPL); dark interference colours; dotted limpidity. Does not exhibit UV fluorescence.

Basic Organic Component c/f_{10 μ m} c/f ratio 80:20

Totals <1%. Coarse fraction dominated by organ residues; yellow (PPL); bright birefringence; exhibits weak UV fluorescence; up to 300 μ m in diameter.

Fine fraction dominated by small (<30 μ m) deposits of red- brown isotropic (rarely larger) fragment.

Groundmass

Inorganic; red-brown (PPL); little birefringence; stipple- speckled b-fabric; gives an overall porphyric related distribution pattern.

Pedofeatures

Total $\approx 5\%$. Dominated by amorphous and cryptocrystalline pedofeatures as; typic nodules, strongly to moderately impregnated with good contrast; occasionally surround compound rock fragments; up to 1.5mm in diameter; red-brown (PPL); red-orange birefringence; occasionally as red-brown pure isotropic nodules.

Textural pedofeatures are pale yellow, birefringent typic coatings up to 20 μ m thick.

BC (Vertical section)

Microstructure

Strongly to moderately developed pedality. Peds total $\approx 80\%$ as ultrafine to very fine subangular to angular blocky peds; undulating partially accommodated surfaces; random distribution.

Porosity is 15%. Inter-aggregate voids as complex packing voids; up to 1mm in diameter; stretch for several cm's; straight crack pattern; undulating and partially accommodated surfaces; random distribution; become more vughy where coarse single mineral grains dominate.

Basic Mineral Component c/f_{10 μ m} c/f ratio 65:35

Coarse fraction dominated by Silurian siltstone fragments: total 50%; oblate smooth to undulating rounded; random distribution; $>4\text{cm}$; often exhibit pellicular to thick pellicular alteration and planar cracks. Single mineral grains; up to $90\mu\text{m}$; largest dominated by oblate to equant smooth angular to subangular quartz grains; occasionally exhibit polycrystallinity or undulose extinction; random distribution; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with rare rutile, zircon and tourmaline).

Fine fraction: pale brown (PPL); inorganic; dark interference colours; dotted limpidity.

Basic Organic component c/f ratio 50:50

Totals $<1\%$. Coarse fraction occurs as; (a) organ residues with bright birefringence; always associated with voids; exhibit UV fluorescence; (b) tissue residues, often embedded in the matrix; dark brown (isotropic) to black; .

Fine fraction occurs as dark brown (isotropic)/black dense complete void infillings.

Groundmass

Inorganic; red-brown (PPL); little birefringence; stipple-speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Total $<1\%$; composed of (a) nodules towards the top of the horizon as it merges with the Bs

(b) Textural pedofeatures as impure clay typic coatings, occasionally stained red-brown although aggregate extinction features still visible; also as pale yellow, birefringent typic coatings up to $20\mu\text{m}$ thick.

BC (Horizontal section)

Microstructure

Peds total >80%. Dominated by ultrafine to fine angular blocky peds; undulating accommodated to partially accommodated surfaces; random distribution.

Porosity is ≈15-20%. Inter-aggregate voids as complex packing voids; up to 1mm in diameter; undulating partially to fully accommodated surfaces; as C grades into Bs voids become more medium to coarse meso vughy with smooth to undulating unaccommodated surfaces; random distribution; rare intra- aggregate voids occur as coarse-micro packing voids; smooth to undulating accommodated surfaces.

Basic Mineral Component c/f_{10μm} c/f ratio 70:30

Coarse fraction dominated by Silurian siltstone fragments: total 50%; oblate to prolate smooth subangular; up to several cm's; commonly have planar voids through them with smooth to undulating accommodated surfaces. Single mineral grains; up to 500μm; largest dominated by oblate undulating subangular quartz grains; occasionally exhibit polycrystallinity or undulose extinction; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with few grains of rutile, zircon and tourmaline).

Fine fraction: inorganic; red-brown (PPL); little birefringence; does not exhibit UV fluorescence.

Basic Organic Component c/f ratio 50:50

Totals <1%. Coarse fraction dominated by organ residues; yellow-brown (PPL); bright birefringence; exhibit UV fluorescence; always occur with voids; up to 500μm in diameter.

Fine fraction occurs as; (a)black deposits; up to 400μm; often fully embedded in the soil matrix; (b) red-brown isotropic deposit.

Groundmass

Inorganic; red-brown (PPL); little birefringence; stipple- speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Total <1%. Towards the top of the horizon are dominated by amorphous and cryptocrystalline pedofeatures comprised of typic red-brown strongly to moderately impregnated nodules with red- orange birefringence; lower down textural pedofeatures dominate as; (a)typic coatings of limpid clay; dark brown (PPL); yellow- orange birefringence; typical aggregate extinction features; (b)similar characteristics but embedded in the groundmass; (c) dusty to impure clay, embedded in the matrix but with good contrast.

Appendix IVe Morphological and micromorphological description of a brown podzolic soil (Manod series) from the Hiraethog Moors.

Horizon & Depth (cm)	Description
Oh (0-2cm)	Undecomposed grass stems and roots; clear boundary.
A _h (2-11cm)	Dark brown (10YR 3/3)loamy textured material with strongly developed fine granular peds; very slightly stoney, siltstone fragments up to 5cm in size; grass roots penetrate throughout the horizon; clear sharp boundary.
B _s (11-28cm)	Yellow-brown (10YR 5/8) horizon, silty sandy textured, frequent stones which lack noticeable preferred orientation; strongly developed granular pedality; dry; common roots; gradual boundary; at 20cm an oval shaped feature occurs, dark brown (10YR 5/8)in colour and lacking the concentration of stones found in the surrounding material; has a more clay silt loam texture.
C (28-)	Very pale brown (10YR 7/4), very stoney, up to 10cm in size with some preferred orientation, gradual boundary;dry; medium granular peds; pedality moderately developed; few roots.

A_h (Vertical section)

Microstructure

Pedality moderately developed. Peds occur as: (a) ultrafine to very fine angular blocky peds; smooth to undulating accommodated surfaces; (b) ultrafine spheroidal granules; smooth unaccommodated surfaces; random distribution.

Porosity is 25-30%. Inter-aggregate voids: (a) associated with blocky peds are complex packing voids; smooth to undulating accommodating surfaces; up to 800 μ m; (b) associated with granules are complex packing voids; undulating unaccommodating surfaces with a more strongly developed pedality; voids have a random distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 15:85

Coarse fraction totals <10%. (a) Silurian siltstone fragments; oblate smooth rounded; up to 3cm; occasionally include planar voids with smooth accommodating surfaces. (b) Single mineral grains total <5%; dominated by oblate smooth subrounded quartz grains; up to 100 μ m; occasional mica flakes and chlorite grains; random distribution.

Fine fraction: organo-mineral; yellow-brown (PPL); dotted limpidity; dark birefringence.

Basic Organic Component c/f ratio 15:85

Coarse fraction totals \approx 5%. Organ residues, pale yellow (PPL); white interference colours; usually circular but can be elongated; always associated with void spaces, exhibits weak Uv fluorescence.

Organic fine material: (a) black, embedded in the matrix; random distribution (dominant form); (b) pale yellow deposits within voids; usually isotropic; occasionally exhibiting weak birefringence; (c) orange-red dense incomplete void infillings; occasionally exhibit aggregate extinction features.

Groundmass

Organo-mineral; pale to dark brown (PPL); little birefringence; dotted limpidity.

Pedofeatures

Total <1%. Dominated by amorphous and cryptocrystalline pedofeatures: (a) See organic fine material; (b) Typic nodules; weakly to moderately impregnated; orange-red (PPL); red-brown interference colours; up to 800 μ m in diameter.

A_h (Horizontal section)

Microstructure

Pedality moderately developed, becoming strongly developed where granules dominate. Ped occur as: (a) ultrafine to very fine angular blocky peds; undulating accommodated surfaces; (b) ultrafine spheroidal granules; smooth to undulating unaccommodating surfaces; clustered distribution.

Porosity is 40–45%. Inter-aggregate voids as: (a) complex packing voids; undulating accommodated surfaces associated with blocky peds; (b) complex packing voids with undulating unaccommodated surfaces associated with granules.

Basic Mineral Component c/f_{10μm} c/f ratio 15:85

Silurian siltstone fragments: up to 1mm; oblate smooth subrounded; occasionally exhibit pellicular to thick pellicular alteration. Single mineral grains: up to 150μm; dominated by oblate to equant smooth subangular quartz grains; occasional mica flakes and chlorite grains. All coarse fraction has a random distribution.

Fine fraction: organo-mineral; brown (PPL); little birefringence; dotted limpidity.

Basic Organic Component c/f ratio 10:90

Fine fraction totals ≈3%: (a) black, usually embedded within matrix; (b) pale yellow, isotropic; dense complete void infillings; where laminated gives weak birefringence and weak UV fluorescence; (c) red-brown isotropic dense complete/incomplete void infillings; often with planar cracks with accommodating surfaces; (d) pigmentation of the mineral matter (dominant form).

Coarse fraction always associated with voids Organ residues: several cm's in size; pale yellow (PPL); white interference colours; usually circular; some cells exhibit perfect aggregate extinction crosses.

Groundmass

Organo-mineral; brown (PPL); little birefringence.

Pedofeatures

Amorphous and cryptocrystalline pedofeatures dominate, as described in the organic fine material.

Excretion pedofeatures: near rounded; clustered basic distribution; organo-mineral; red-brown (PPL); little birefringence; show signs of aging *ie* coalescence.

B_{s1} (Vertical section)

Microstructure

Peds: (a) ultrafine spheroidal crumbs; undulating unaccommodating surfaces; clustered distribution; strongly developed pedality: (b) ultra fine to very fine sub-angular blocky peds; undulating to rough partially accommodated surfaces; random distribution; moderately developed pedality.

Porosity is $\approx 20\%$. (a) Associated with blocky peds are complex packing voids; up to 800 μm wide; undulating to rough partially accommodated surfaces: (b) associated with crumbs are complex packing voids; rough unaccommodating surfaces.

Basic Mineral Component c/f_{10 μm} c/f ratio 40:60

Silurian siltstone fragments: total $\approx 20\%$; equant to oblate smooth subrounded to sub angular; occasionally exhibit pellicular alteration. Single mineral grains: up to 200 μm ; largest dominated by equant smooth subangular quartz grains occasionally exhibiting undulose extinction; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with rare tourmaline and zircon).

Fine fraction: inorganic; pale red-brown (PPL); grey-brown interference colours; dotted limpidity.

Basic Organic Component c/f ratio 75:25

Coarse fraction totals $\approx 3\%$. Dominated by organ residues up to 1cm; black (PPL); occurring in voids and embedded in matrix. Tissue fragments; black; embedded in the matrix.

Fine fraction totals 1% as black material fully embedded within the matrix; or orange isotropic dense complete void infillings.

Groundmass

Inorganic, pale red-brown (PPL); grey-brown birefringence; stipple-speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Total $< 1\%$.

(a) Amorphous and cryptocrystalline pedofeatures as typical moderately to strongly impregnated nodules; up to 500 μm in diameter; prominent contrast.

B_{s1} (Horizontal section)

Microstructure

Peds: (a) Ultrafine to very fine subangular to angular blocky peds; undulating to rough partially accommodating surfaces; moderately to strongly developed pedality; random distribution. (b) Ultrafine spheroidal crumbs; undulating unaccommodated surfaces; clustered distribution.

Porosity is $\approx 30\%$. Complex packing voids (up to 2mm in width); undulating to rough partially accommodated surfaces; random distribution.

Basic Mineral Component c/f_{10 μ} c/f ratio 60:40

Silurian siltstone fragments: total $>20\%$; oblate to prolate smooth subangular; up to 1cm; occasionally show pellicular alteration; random distribution. Single mineral grains: up to 700 μm ; largest dominated by oblate to equant undulating to smooth subangular quartz grains; occasionally polycrystalline or exhibit undulose extinction; remainder composed of quartz grains, feldspars, mica flakes and heavy minerals (chlorite with rare tourmaline and zircon).

Fine fraction: inorganic; pale-brown (PPL); dark grey-brown interference colours; dotted limpidity.

Basic Organic Component c/f ratio 50:50

Totals $<2\%$. Coarse fraction: (a) organ residues as very pale yellow (PPL) circular residues; white interference colours; only occur in voids; (b) tissue residues as black material; often embedded in the matrix.

Fine fraction; red-brown (isotropic) to black deposits; usually embedded in the matrix.

Groundmass

Inorganic; pale red-brown (PPL); grey-brown interference colours; dotted limpidity; stipple speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Total $<1\%$. Dominated by amorphous and cryptocrystalline pedofeatures as red-brown typical to amiboidal strongly impregnated nodules; orange-red interference colours; up to 800 μm in diameter; random distribution.

B_s2 (Vertical section)

Microstructure

Moderately to strongly developed pedality. Peds: (a) ultrafine to very fine subangular to angular blocky peds; undulating partially accommodating surfaces (b)occasional ultrafine spheroidal crumbs; undulating unaccommodating surfaces; clustered distribution.

Porosity is ~15%. Inter-aggregate voids: (a) complex packing voids; up to 1mm in diameter; undulating partially accommodated surfaces; random distribution; (b)occasional fine- macro vesicles; smooth unaccommodating surfaces; clustered distribution.

Basic Mineral Component c/f_{10μm} c/f ratio 65:35

Coarse fraction: dominated by Silurian siltstone fragments; (~40%); oblate to prolate undulating subrounded; 0.5-5cm; rarely exhibit pellicular alteration. Single mineral grains: up to 150μm; largest dominated by prolate to oblate smooth subrounded quartz grains occasionally exhibiting polycrystallinity or undulose extinction; remainder composed of quartz grains, feldspars, mica flakes and heavy minerals (chlorite with rare tourmaline and zircon).

Fine fraction ; inorganic, red-brown (PPL); grey-brown birefringence; dotted limpidity.

Basic Organic Component c/f ratio 40:60

Coarse fraction: (a) organ residues: always occurring in void spaces; pale yellow (PPL); white-grey interference colours; circular or elongated; random distribution; (b)tissue residues; black, usually embedded in the matrix.

Fine fraction: dominated by black deposits embedded in the matrix.

Groundmass

Inorganic; pale red-brown (PPL); stipple-speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Amorphous and cryptocrystalline pedofeatures; red-brown typic nodules with orange-red interference colours, moderately to strongly impregnated.

Textural pedofeatures; often on upper surface of peds as; (a)thin (<30μm) typic void coatings of dusty/impure clay, red- brown (PPL), yellow orange interference colours, exhibit aggregate extinction features; (b)complete dense void infillings of impure clay, red-brown (PPL), yellow-orange birefringence; aggregate extinction features.

B_s2 (Horizontal section)

Microstructure

Moderately to strongly developed pedality. Peds dominated by ultrafine to very fine subangular to angular blocky peds; smooth to undulating partially accommodated surfaces; ; random distribution.

Porosity is $\approx 20\%$. (a) Dominated by complex packing voids; smooth to undulating partially accommodated surfaces, up to 5mm; (b) occasional fine-macro vughs; random distribution.

Basic Mineral Component c/f₁₀ μm c/f ratio 70:30

Silurian siltstone fragments: up to 3cm; oblate to equant smooth subangular; occasionally show pellicular alteration; frequently have planar cracks with partially accommodated surfaces; random distribution. Single mineral grains; up to 700 μm ; largest dominated by equant undulating subangular quartz grains, often exhibiting polycrystallinity or undulose extinction; remainder composed of quartz grains, feldspars, mica flakes and heavy minerals (chlorite with rare zircon and epidote).

Fine fraction

Basic Organic Component c/f ratio 100:0

Totals <1%. Dominated by coarse fraction (a) Organ residues: pale yellow (PPL); white/grey interference colours; always situated within void spaces; or black isotropic material embedded in the matrix; (b) tissue fragments: black, embedded in the matrix.

Organic fine material is black; all organic matter has a random distribution.

Groundmass

Inorganic, pale red-brown (PPL); stipple-speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Totals <1%.

(a) Amorphous and cryptocrystalline pedofeatures as red- brown nodules up to 500 μm in diameter; orange-red birefringence; strongly to moderately impregnated; random distribution.

(b) Textural pedofeatures as impure clay typic coatings; up to 40 μm thick; yellow-brown (PPL); yellow-orange interference colours; typical aggregate extinction features; also as similar coatings lining the planar cracks of compound rock fragments.

BC (vertical section)

Microstructure

Pedality is moderately to weakly developed. Peds comprise 80% as ultrafine to very fine subangular blocks with few ultrafine spheroidal crumbs, often as possible coalesced smaller crumb peds; undulating partially accommodated surfaces; blocks have a random distribution, crumbs a clustered basic distribution.

Porosity is 20%. Interaggregate voids as complex packing voids up to 500µm in diameter with a straight crack pattern and random basic distribution and undulating partially accommodated surfaces. Few vughs up to 500µm in diameter occur with smooth unaccommodated surfaces.

Basic Mineral component c/f_{10µm} c/fratio 70:30

Coarse component is dominated by Silurian siltstone fragments totalling 50%; oblate smooth rounded to subrounded with occasional planar cracks through them. Single mineral grains up to 100µm in diameter occur of oblate to equant smooth angular to subangular quartz, occasionally exhibiting polycrystallinity or undulose extinction, remainder composed of mica flakes, feldspars and heavy minerals (chlorite, rutile, tourmaline and zircon).

Fine fraction is inorganic, brown with dark-grey interference colours; speckled limpidity.

Basic organic component c/f ratio 50:50

Totals <1%. Coarse fraction composed of yellow-brown tissue residues up to 200 µm in diameter with yellow-orange interference colours and are always associated with void spaces; exhibit UV auto-fluorescence.

Fine fraction occurs as dark-brown/black dense complete void infillings.

Groundmass

Inorganic, red-brown with dark-grey interference colours, stipple-speckled giving an overall porphyric related distribution pattern.

Pedofeatures

Total <1% as (a) cryptocrystalline pedofeatures as typic moderately impregnated nodules, red-brown with orange interference colours; rare halos.

(b) Textural pedofeatures as impure clay typic void coatings or dense complete void infillings, red-brown with yellow-orange interference colours giving aggregate extinction.

BC (Horizontal section)

Microstructure

Pedality is moderately developed. Peds total 75% as ultrafine to very fine subangular blocks with few ultrafine spheroidal crumbs which are often coalesced into larger porous units; undulating partially accommodated surfaces; blocks have a random basic distribution, crumbs a clustered basic distribution.

Porosity is 25% as complex packing voids up to 500 μ m in diameter with undulating partially accommodated surfaces.

Basic Mineral component c/f_{10 μ m} c/fratio 70:30

Coarse component is dominated by Silurian siltstone fragments totalling 50%; oblate smooth rounded to subrounded with occasional planar cracks through them. Single mineral grains up to 100 μ m in diameter occur of oblate to equant smooth angular to subangular quartz, occasionally exhibiting polycrystallinity or undulose extinction, remainder composed of mica flakes, feldspars and heavy minerals (chlorite, rutile, tourmaline and zircon).

Fine fraction is inorganic, brown with dark-grey interference colours; speckled limpidity.

Basic organic component c/f ratio 50:50

Totals <1%. Coarse fraction composed of yellow-brown tissue residues up to 200 μ m in diameter with yellow-orange interference colours and are always associated with void spaces; exhibit UV auto-fluorescence.

Fine fraction occurs as dark-brown/black dense complete void infillings.

Groundmass

Inorganic, red-brown with dark-grey interference colours, stipple-speckled giving an overall porphyric related distribution pattern.

Pedofeatures

Total <1% as (a) cryptocrystalline pedofeatures as typical moderately impregnated nodules, red-brown with orange interference colours; rare halos.

(b) Textural pedofeatures as impure clay typical void coatings or dense complete void infillings, red-brown with yellow-orange interference colours giving aggregate extinction. Occasionally occur fragmented with rounded edges.

Fossil(?) Mole Channel

Microstructure

Pedality strongly developed. Peds dominated by ultrafine spheroidal granules; smooth unaccommodating surfaces; random distribution; sometimes coalesced into ultrafine to very fine subangular to angular blocky peds with undulating partially accommodated surfaces.

Porosity is $\approx 30\%$. Compound packing voids: undulating partially accommodated to unaccommodated surfaces; random distribution; where peds aggregated intra-aggregate voids occur as fine- to coarse-micro vughs with undulating unaccommodated surfaces.

Basic Mineral Components c/f_{10 μ m} c/f ratio 20:80

Silurian siltstone fragments; up to 4cm; oblate to equant smooth subrounded to sub angular; random distribution; commonly exhibit planar cracks with smooth to undulating accommodated surfaces. Single mineral grains: up to 150 μ m; largest dominated by oblate to equant smooth subangular quartz grains occasionally exhibiting polycrystallinity or undulose extinction; remainder composed of quartz grains, amphiboles, mica flakes and heavy minerals (chlorite with rare rutile, zircon and tourmaline).

Fine fraction: organo-mineral; brown (PPL); dark interference colours; dotted limpidity.

Basic Organic Component c/f_{10 μ m}

Fine fraction dominated by organic pigmentation; also as as black isotropic deposits embedded in the matrix, or orange-red isotropic dense incomplete void infillings.

Coarse fraction as pale yellow isotropic deposits; white interference colours; always associated with voids.

Groundmass

Organo-mineral; brown (PPL); stipple-speckled b-fabric giving an overall porphyric related distribution.

Pedofeatures

Textural Pedofeatures:

(a) Dense incomplete void infillings, yellow-brown (PPL); dark interference colours showing occasional small (<20 μ m) birefringent speckles; composed of fine material with silt-sized inclusions.

(b) Yellow-brown typic coatings $\approx 15\mu$ m thick with yellow interference colours exhibiting perfect aggregate extinction cross.

Appendix IVf Morphological and micromorphological description of a stagnohumic gley soil profile (Freni series, formally the Ynys series).

Horizon & Depth (cm)	Description
L (0-6)	Dark yellowish brown (10YR 4/4), fresh, loose litter almost entirely of recognisable plant remains.
F/H (6-8)	Dark greyish brown (10YR 3/2), partly decomposed or comminuted litter with some darker more humified material; fewer plant remains recognisable; gradual boundary.
Oh (8-32)	Dark black (7.5YR 2/0) horizon consisting of amorphous peat with no visible plant remains; stays moist most of the year; no recognisable plant remains except for roots which penetrate the whole depth of the horizon; contains few (<1%) mineral grains of siltstone; on drying out it forms fine to medium prismatic/columnar peds; gradual boundary.
Oh (32-41)	Dark greyish brown (10YR 4/2) composed of amorphous peat with a component of mineral matter in the form of fine silts; has an abrupt boundary; few plant remains recognisable except fragments of wood up to 10cm in size; large fragments lie directly on the underlying horizon.
E_{ag} (41-52)	Light brownish grey (10YR 6/2) with a gradual boundary; mineral in nature with frequent root channels penetrating the horizon; very fine to medium distinct to prominent mottling common around these channels; few stones occur, those present being soft and angular; little structural development even when completely dry; becomes light grey (10YR 7/1) with depth.
B_g (52-68)	Light grey (10YR 7/1) with a clear boundary; fewer root channels; very fine to fine prominently mottled; occasional stones, soft, angular in form; no structural development even when completely dry.
BC_g (68-97)	Light grey (10YR 7/1), clay with few root channels occurring, very fine to medium distinct to prominent mottles common along channels; when dry produces some large (>10cm, coarse-v. coarse) prismatic and columnar peds; little other structural development; siltstone fragments more common, up to 5cm in size.

O_k (Vertical section)

Microstructure

Pedality strongly developed. Peds total $\approx 70\%$; dominated by ultrafine to very fine subangular blocky peds; unaccommodated surfaces; some ultrafine spheroidal crumb peds total $< 5\%$ ped area; random distribution.

Porosity is $\approx 30\%$. Inter-aggregate voids: compound packing voids; rough unaccommodating walls; up to 1mm in diameter; random distribution. Intra-aggregate voids: coarse micro-voids; undulating unaccommodating surfaces; random distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 30:70

Silurian siltstone fragments: up to 1200 μ m; oblate to prolate rough to undulating subangular; total $< 2\%$. Single mineral grains total $\approx 5\%$; up to 100 μ m; largest dominated by oblate to equant smooth subrounded grains of quartz; occasional chlorite grains, mica fragments and rare tourmaline grains; random distribution.

Fine fraction: totals $\approx 3\%$; inorganic dense incomplete void infillings of pale grey fine silts and clays with included large fragments; little interference; speckled limpidity.

Basic Organic Component c/f ratio 15:85

Coarse fraction: (a) organ residues: up to 1500 μ m; pale yellow-brown; bright interference colours; also as black residues; up to 500 μ m in diameter with two thin-walled cell types; (b) tissue residues: up to 300 μ m; black; all coarse fraction has a random distribution.

Organic fine material: (a) black; up to 100 μ m; often embedded in soil matrix; (b) red-brown isotropic dense incomplete void infilling; can occur as thin ($\approx 40\mu$ m) strands within voids giving yellow-orange interference colours; (c) pale brown isotropic material making up the matrix of the soil; (d) rare pollen grains (*Betula*) occur embedded in the matrix.

Groundmass

Organic; pale brown (PPL); isotropic; occasional small ($< 40\mu$ m) birefringent areas; with white/grey interference colours.

Pedofeatures

None.

O_h (Horizontal Section)

Microstructure

Pedality moderately to strongly developed. Peds total 60-70% as (a) ultrafine to very fine subangular blocks; (b) ultrafine spheroidal crumb peds; surfaces are rough and unaccommodated; random distribution.

Porosity is 30-40%. Compound packing voids with rough unaccommodated surfaces (inter-aggregate voids); up to 1mm in width; extend for several mm's. Intra-aggregate voids as coarse- micro vughs; undulating unaccommodated surfaces; random distribution.

Basic Mineral Component c/f_{10μm} c/f ratio 80:20

Silurian siltstone fragments: total <1%; up to 200μm; oblate undulating sub-rounded; random distribution. Single mineral grains: up to 100μm; dominantly oblate to equant undulating sub- rounded quartz fragments; random distribution; occasional mica flakes and chlorite grains.

Fine fraction: inorganic; recognisable only as small (<10μm) birefringent areas within the organic groundmass.

Basic Organic Components c/f ratio 10:90

Coarse fraction totals <5% as (a) organ residues: yellow-brown structures; up to 1mm; yellow-orange interference colours; always occur in voids; random distribution; also as black structures; (b) tissue residues: dominantly black; embedded in soil matrix; up to 400μm in diameter.

Fine fraction dominated by a pale brown, isotropic amorphous groundmass; also as (a) pale yellow laminated deposit; orange- yellow interference colours; (b) black fragments embedded in the matrix; (c) red-brown isotropic incomplete void infilling.

Groundmass

Inorganic with occasional inclusions of inorganic silts and fine sands. Brown in PPL and isotropic.

Pedofeatures

None.

E_{ag} (Vertical section)

Microstructure

Pedality moderately developed. Peds dominantly very fine subangular blocky; few accumulations of ultrafine crumb-like spheroidal peds with a clustered basic distribution pattern (see excretion pedofeatures); surfaces rough to undulating; usually unaccommodated; random distribution.

Porosity is 20%. Inter-aggregate voids: complex packing voids; rough to undulating, unaccommodated surfaces; random distribution. Intra-aggregate voids: <5%; consist of medium-micro vughs; undulating walls; random distribution.

Basic Mineral Components c/f_{10μm} c/f ratio 20:80

Silurian siltstone fragments: total ≈2%; up to 100μm; oblate smooth subangular; random distribution. Single mineral grains range from 10-120μm; largest dominated by quartz, oblate subangular and occasionally polycrystalline; remainder composed of quartz grains, feldspars and heavy minerals (chlorite with rare zircon, tourmaline and epidote); random distribution.

Fine fraction: brown coloured (PPL) due to pigmentation by organic matter; speckled limpidity; dark grey in XPL; weak UV fluorescence occurs as small circular to oval structures.

Basic Organic Components. c/f ratio 25:75

Coarse fraction: tissue residues; up to 1mm; dark brown (isotropic) to black.

Fine fraction: dominated by organic pigmentation of the mineral matter; red-brown (PPL); little interference colours. Remaining organic fine material occurs as; (a) red-brown deposits commonly associated with void surfaces; (b) infillings of smaller voids, isotropic, occasionally cracked to produce accommodated, smooth walled planar voids; (c) accumulations within voids, pale yellow, showing some laminations and weak pale-yellow UV fluorescence.

Groundmass

Organo-mineral; stipple-speckled b-fabric; exhibiting some UV fluorescence.

Pedofeatures

(a) See fine organic material.

(b) Few shaped excrement pedofeatures within voids, possibly of Julidae or Glomerdae origin, some coalescence to form a porous mass; occur as incomplete void infillings.

Eag (Horizontal section).

Microstructure

Moderately developed pedality; weakly to moderately developed where less discrete fine organic accumulations; peds total $\approx 80\%$; dominated by ultrafine to very fine sub-angular blocks; unaccommodated and rough to undulating surfaces; smoother in areas of lower organic matter; random distribution.

Porosity is $\approx 20\%$. Inter-aggregate voids: compound packing voids; rough to smooth undulating surfaces; up to $300\mu\text{m}$ in diameter; random distribution; with lower levels of organic matter occasional vesicles occur.

Basic Mineral Component c/f_{10 μm} c/f ratio 30:70

Silurian siltstone fragments: total $< 2\%$; up to $500\mu\text{m}$; oblate, undulating rounded. Single mineral grains; up to $200\mu\text{m}$; larger ($> 40\mu\text{m}$) dominated by subrounded smooth quartz grains, occasionally polycrystalline; remainder composed of quartz grains, mica flakes and heavy minerals (chlorite with rare zircon, tourmaline, rutile).

Fine fraction: organo-mineral; brown (PPL); dark grey in XPL; dotted limpidity; exhibits weak UV fluorescence as small fine isotropic organic accumulations or shell-like structures which are commonly deformed.

Basic Organic Component c/f ratio 30:70

Organ residues: occur within voids; up to 1mm ; black structures or red-brown structures with birefringence. Tissue residues also of similar appearance; or residues up to 2mm in diameter, red-brown to yellow (PPL) and isotropic (phlobaphane containing tissue); random distribution.

Fine material: (a) red-brown isotropic deposits in association with voids and void surfaces; can occur with tissue residues and grade into them; (b) yellow-brown laminated deposit; exhibits some birefringence and weak UV fluorescence; if unlaminated and occurs as a dense complete void infilling then does not exhibit UV fluorescence (c) organic pigmentation occurs throughout the groundmass giving it a general brown colouration; darker pigmentation occurs around voids as typical hypocoatings, especially where the soil is more dense with less void area.

Groundmass

Organo-mineral; fine silts and clays stained brown by organic matter; stipple-speckled b-fabric giving an overall porphyric related distribution.

Pedofeatures

Amorphous and cryptocrystalline pedofeatures as typical hypocoatings of voids; red-brown; associated with organic material; red-orange in XPL. Also organic fine material as described above.

B_g (Vertical section)

Microstructure

Weak to moderately developed pedality; dominated by ultrafine to very fine subangular to angular blocky peds; smooth to undulating surfaces; random distribution.

Porosity is 20%. Inter-aggregate voids: towards the top of the horizon - fine to medium-meso vesicles, medium to coarse-meso vughs and complex packing voids; up to 300 μ m; random distribution; with depth % increases as planar voids with smooth accommodating walls, extending for several cm's; have a zig-zag crack pattern with an inclined orientation (moderately orientated); basic linear distribution.

Basic Mineral Component c/f_{10 μ m} c/f ratio 40:60

Silurian siltstone fragments: <10%; up to 1cm; some exhibit sharp contrast; oblate smooth rounded; frequently show complete alteration; often exhibit cracking as planar voids. Single mineral grains up to 100 μ m; largest (>60 μ m) consist of quartz grains, oblate to equant, subrounded to sub-angular, often polycrystalline or exhibiting undulose extinction; remainder composed of quartz, feldspars, mica flakes and heavy minerals (chlorite with rare zircon, rutile, tourmaline and epidote).

Fine fraction: pale grey/brown; fine silts and clays; white to grey interference colours; red-brown colouration occasionally on void surfaces.

Basic Organic Component c/f ratio 30:70

Organic matter totals <5% as (a) coarse fraction: organ residues, yellow- to red-brown (PPL), yellow-orange interference colours; always associated with voids; up to 5mm long; (b) fine fraction: associated with void surfaces as typic coatings/hypocoatings; red-brown (PPL); coatings are isotropic; hypocoatings give red-orange interference colours.

Groundmass

Inorganic; pale grey/brown (PPL); white/grey interference colours; stipple to mosaic-speckled b-fabric giving an overall porphyric related distribution pattern.

Pedofeatures

Total 5%:

(a) Amorphous and cryptocrystalline pedofeatures; always on void surfaces; as typic hypocoatings up to 1mm thick; strong contrast; red-brown (PPL); orange/red (XPL); occasionally associated with organic matter in voids, usually darker in colour in these cases; occasionally as typic quasi-coatings similar in size.

(b) Textural pedofeatures: (1) Embedded in the matrix; up to 30 μ m; consist of dusty clay with aggregate extinction features; (2) as above but with basic banded distribution parallel to planar voids but in the matrix (horizontal in relation to profile orientation); (3) as above but dense incomplete void infillings, (4) typic coatings along planar voids; 20 μ m thick; towards the base of the horizon.

Bg (Horizontal section)

Microstructure

Moderately developed pedality; peds subangular to angular very fine to ultrafine blocks; angularity increases with depth; smooth to undulating partially accommodated surfaces; random distribution.

Porosity is 10%. Inter-aggregate voids: fine to medium meso chambers, macro planar voids and fine-meso vughs (planar voids increasing in proportion with depth); surfaces smooth to undulating partially accommodated; random distribution; planar voids have a relatively straight zig-zag pattern. Intra-aggregate voids: medium-micro vughs; random distribution.

Basic Mineral Component c/f_{10μm} c/f ratio 55:45

Silurian siltstone fragments: (<10%); sometimes completely altered; up to 1cm; oblate, undulating to smooth rounded. Single mineral grains: up to 200μm; largest dominated by equant to oblate undulating subrounded quartz grains, occasionally polycrystalline or exhibiting undulose extinction; remainder composed of quartz grains, feldspars, mica fragments and heavy minerals (chlorite with rare rutile, tourmaline and zircon).

Fine fraction: inorganic; fine silts and clays; pale grey (PPL); white to grey interference colours; dotted limpidity; some red/brown staining associated with void surfaces.

Organic Basic Component c/f ratio 30:70

Coarse fraction: (a) organ residues: up to 1mm; always in voids; red-brown (PPL); exhibit birefringence; (b) tissue residues: red-brown isotropic; usually deformed; always occur in voids. Organic fine material as (a) dark red-brown, isotropic typic void coatings; (b) isotropic; pale yellow; within smaller voids as dense complete infillings; some laminations visible; length fast; exhibits UV fluorescence. Some groundmass stained red-brown around voids containing altered organic material.

Groundmass

Inorganic; pale grey (PPL); white to grey birefringence colours; stipple-speckled fabric giving an overall porphyric related distribution.

Pedofeatures

Total 5%.

(a) Amorphous and cryptocrystalline pedofeatures; associated with voids as typic to hypocoatings; up to 500μm thick; when associated with organic matter are dark red-brown, mostly isotropic but give some red-orange interference colours.

(b) Textural pedofeatures, up to 200μm long as dense complete infillings of smaller voids; of dusty clay; good aggregate extinction patterns; good contrast; small areas embedded in the matrix are less well contrasted; some exhibit slight banding.

BCg (Vertical section)

Microstructure

Pedality very weakly developed; peds as angular to subangular fine to ultrafine blocks; smooth to undulating partially accommodated surfaces; random distribution.

Porosity is <10%. Complex packing voids; range from 100- 500 μ m in width; smooth to undulating partially accommodated surfaces; commonly associated with the surfaces of compound rock fragments. Intra-aggregate voids as medium to coarse- micro vughs; smooth to undulating unaccommodated walls; planar voids occur through rock fragments with smooth undulating accommodated surfaces.

Basic Mineral Component c.f₁₀ μ m c/f ratio 60:40

Silurian siltstone fragments: total \approx 20%; up to 1cm; oblate to equant smooth rounded; often divided by planar voids with smooth to undulating accommodating surfaces; random distribution. Single mineral grains; up to 1400 μ m; largest dominated by subangular quartz grains, occasionally polycrystalline or exhibiting undulose extinction; occasional mica fragments >45 μ m in size; remainder composed of quartz grains, mica flakes, feldspars and heavy minerals (chlorite with some zircon, tourmaline and epidote).

Fine fraction: inorganic; pale grey (PPL); white to grey interference colours.

Basic Organic Component c/f ratio 5:95

Fine organic matter: (a) red-brown isotropic deposit as typic void coatings; (b) yellow dense complete void infillings; slight birefringence; exhibit weak UV fluorescence; associated with the red-brown form is organic pigmentation; red-brown (PPL) giving slightly orange/yellow interference colours. No coarse material.

Groundmass

Inorganic; fine silts and clays; pale grey (PPL); mosaic- speckled b-fabric; gives an overall porphyric related distribution pattern; does not exhibit UV fluorescence.

Pedofeatures

Total \approx 2%:

(a) Amorphous and cryptocrystalline pedofeatures: typic coatings or hypocoatings; red-brown (PPL); coatings are isotropic; hypocoatings give orange/red interference colours;

(b) Textural pedofeatures: pale yellow/grey; exhibit clear aggregate extinction patterns; dusty clay with occasional inclusions of silt sized particles with a random distribution; up to 200 μ m; also occur embedded in the matrix lacking sharp contrast.

BC_g(Horizontal section)

Microstructure

Very weakly developed pedality; peds dominated by very fine to medium subangular blocks; smooth to undulating partially accommodated surfaces; random distribution; rock fragments exhibit internal planar voids with undulating partially accommodated surfaces.

Porosity is <10%. Inter-aggregate voids: vughs and vesicles with some planar voids; sizes range from 50–400µm in diameter; surfaces smooth to undulating; random distribution. Intra-aggregate voids: coarse micro-vughs; smooth to undulating walls; random distribution.

Basic Mineral Component c/f_{10µm} c/f ratio 70:30

Silurian mud and siltstone fragments: total ≈20%; 1-5 cm in size; oblate, smooth rounded to subrounded; random distribution; occasional smooth to undulating partially accommodated planar voids through them. Single mineral grains; up to 1cm ; generally ≈ 400µm; largest dominated by oblate subrounded to subangular quartz fragments; sometimes exhibit polycrystallinity or undulose extinction; remainder composed of quartz grains, plagioclase feldspars, mica flakes and heavy minerals (chlorite with rare zircon, tourmaline, rutile).

Fine fraction: inorganic silts and clays; pale grey (PPL); white to grey interference colours.

Organic Basic Component c/f ratio 60:40

Coarse fraction dominated by tissue residues: red-brown (PPL); exhibit birefringence; always associated with voids; often several structures within one void; up to 800µm. Also dark red- brown structures that are isotropic; again associated with voids.

Organic fine fraction as; (a)red-brown isotropic typic void coatings; (b) red-yellow material with some orange interference colours.

Groundmass

Pale grey (PPL); mosaic-speckled b-fabric; gives an overall porphyric related distribution.

Pedofeatures

Total ≈5%.

(a)Amorphous and cryptocrystalline pedofeatures; in relation to void surfaces as typic hypocoatings, occasional quasi coatings; red-brown with orange-red interference colours; always occur with organic matter in voids; up to 500µm thick.

(b) Textural pedofeatures; dominantly of dusty or impure clay; yellow (PPL) showing aggregate extinction features; as dense incomplete infillings of voids; with red-brown staining overlaying it, (suggesting clay deposition preceded organic matter deposition); or as dense infillings of voids with good contrast; or with low contrast with frequent inclusions of larger grain sizes.

Appendix V

SEM/EDXRA results

- a-d** Analysis of pale yellow birefringent ped coatings from the B_s horizon of the ironpan stagnopodzolic profile.
- e** Analysis of pale yellow isotropoc ped coatings from the B_s horizon of the ironpan stagnopodzolic profile.
- f-h** Analysis of cutans from the BC horizon of the ironpan stagnopodzol profile.
- i-l** Analysis of the B_f horizon from the ironpan stagnopodzolic profile.

NB.

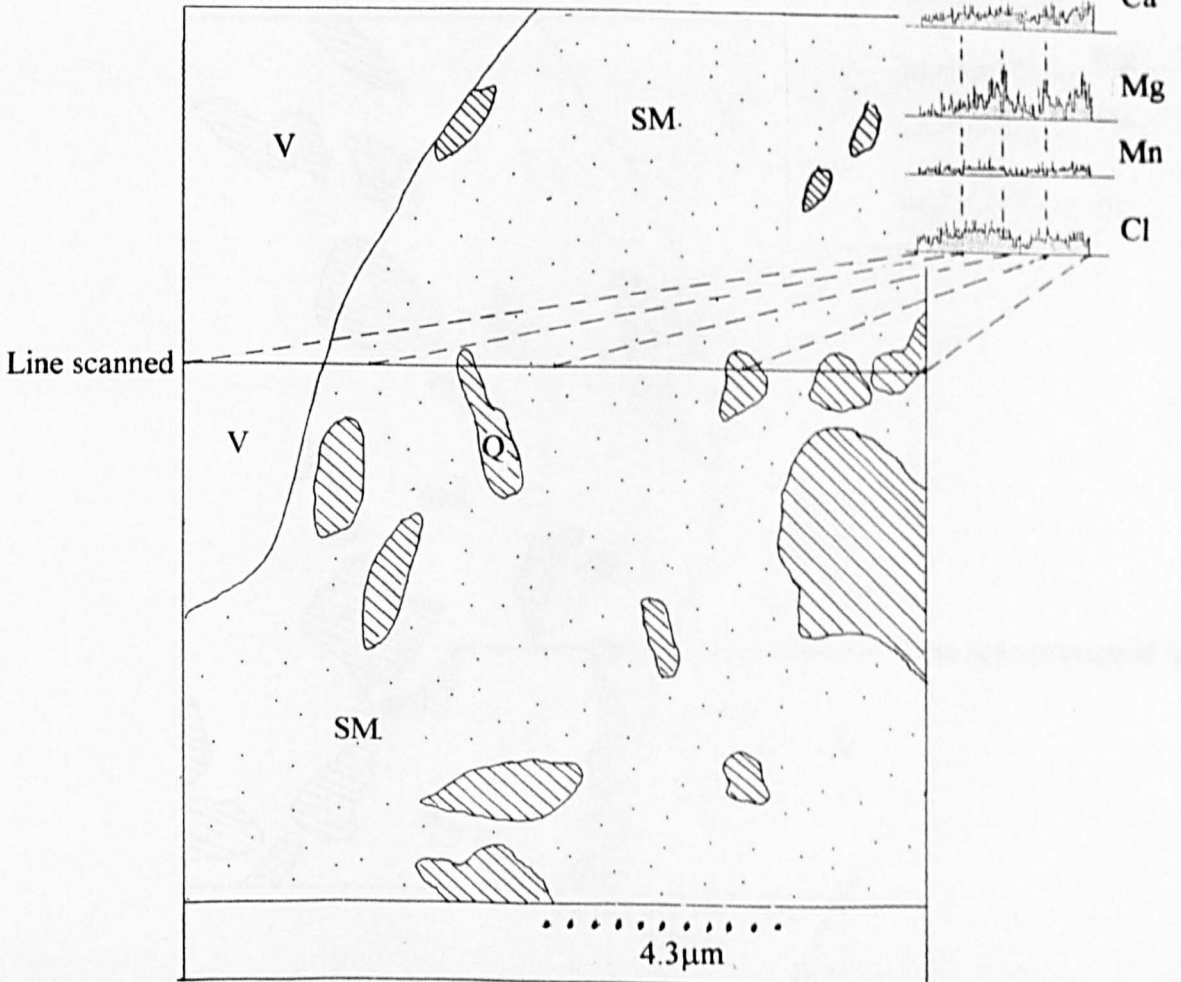
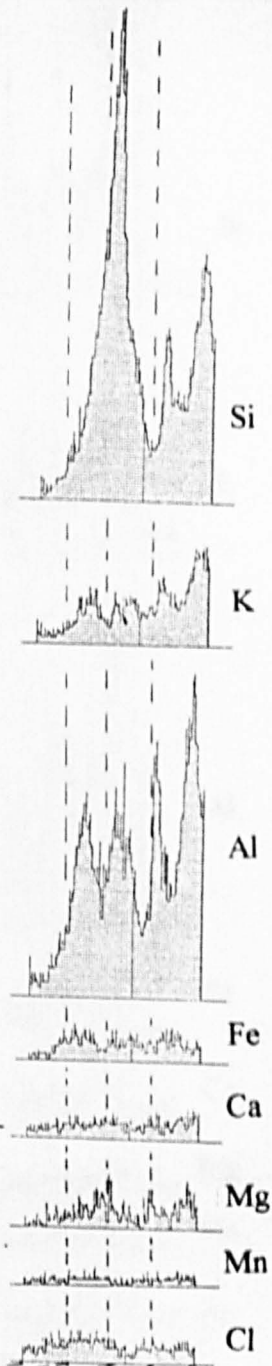
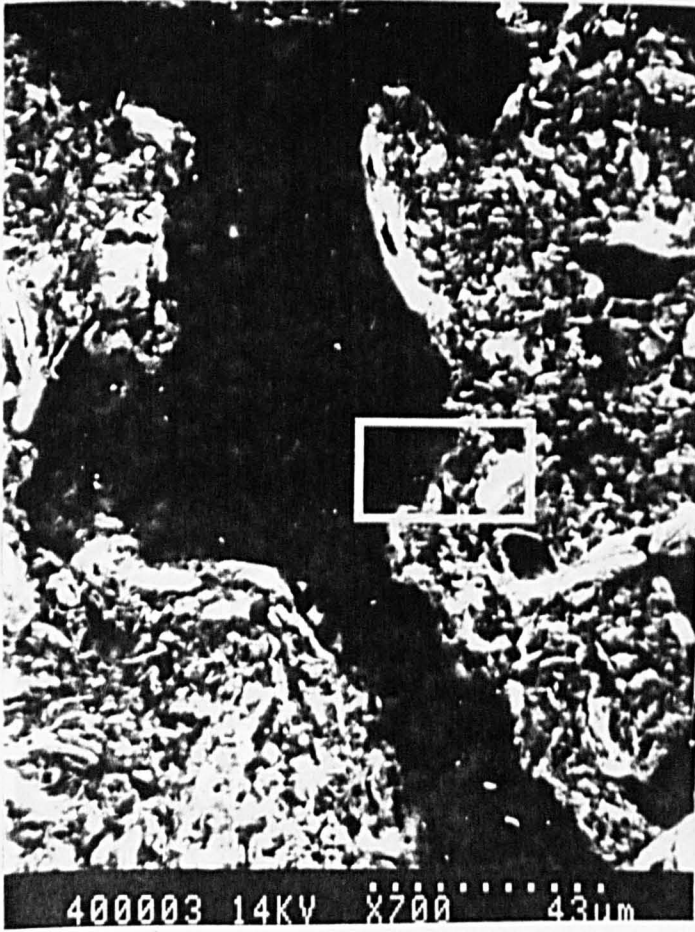
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SM = soil matrix

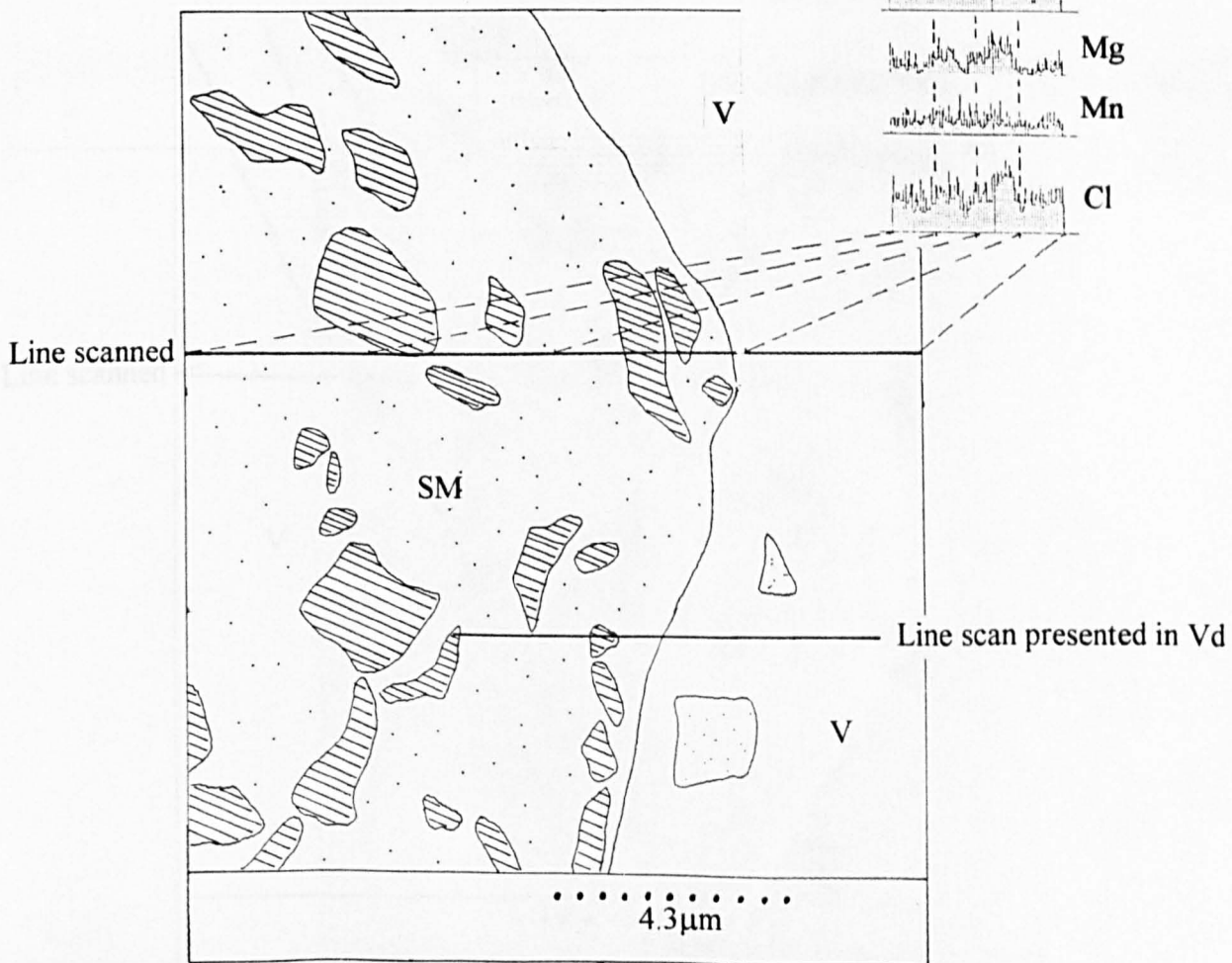
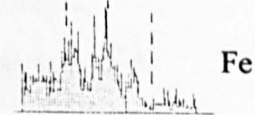
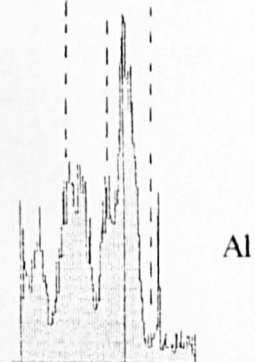
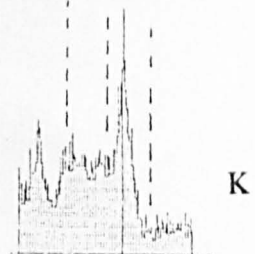
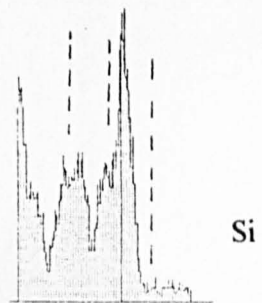
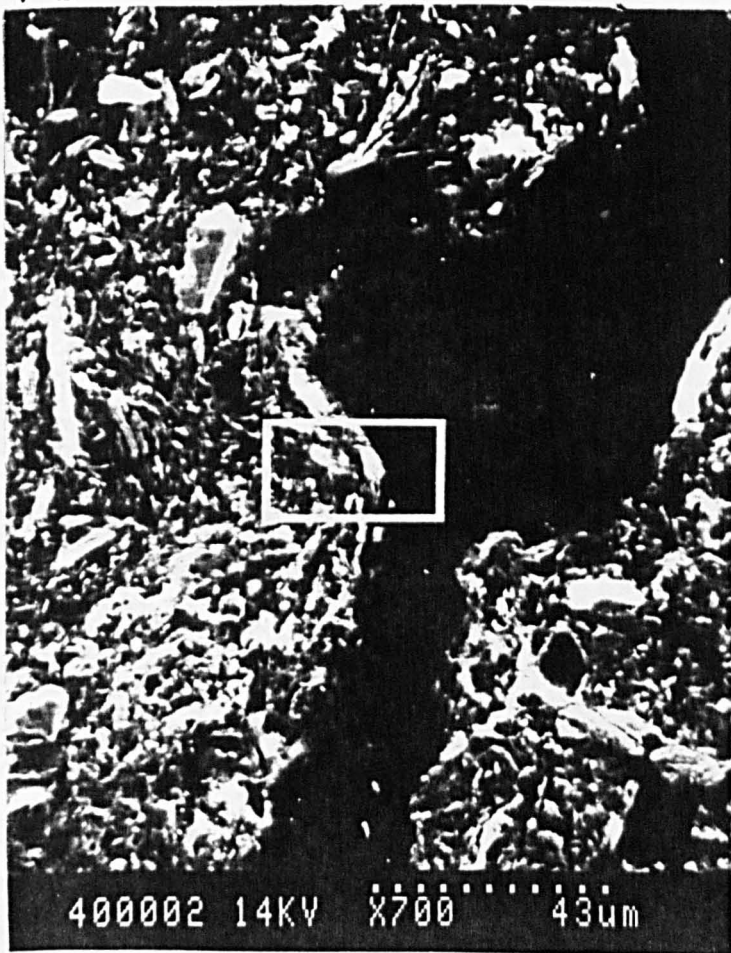
/// = grain

Q = quartz

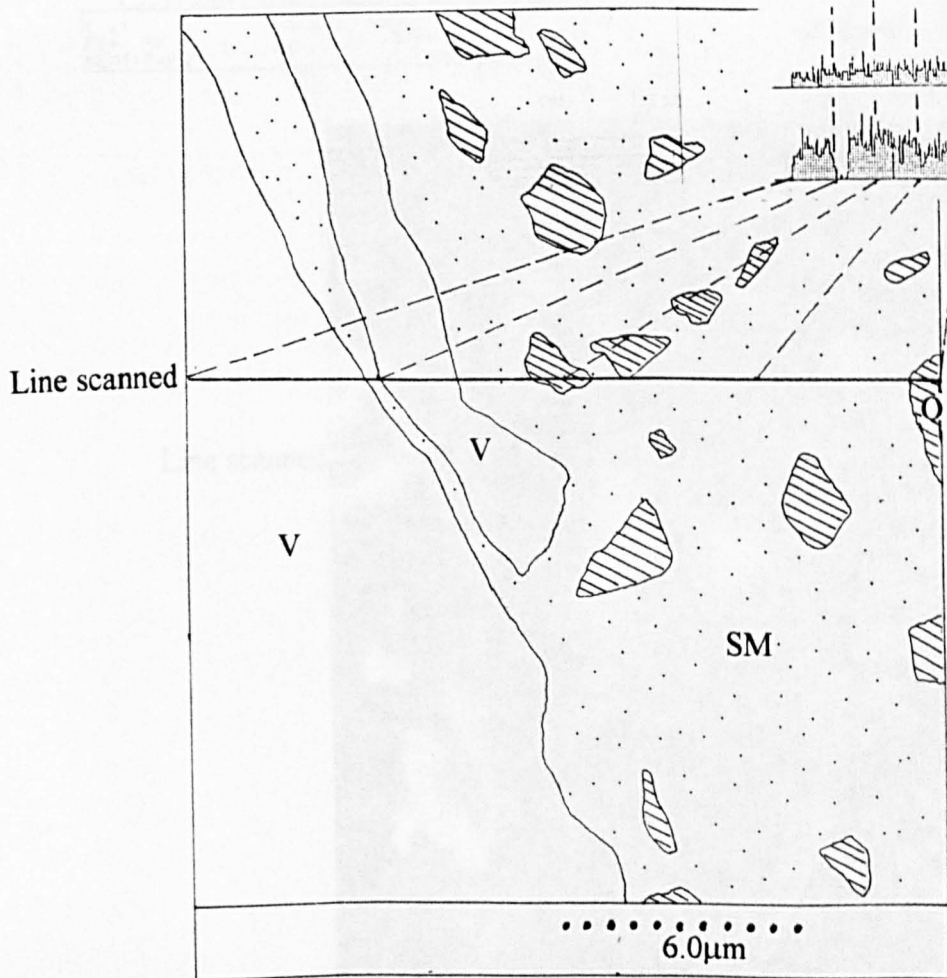
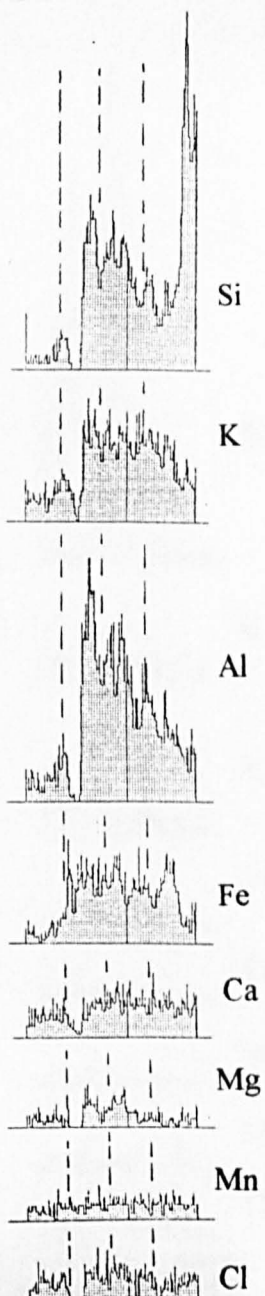
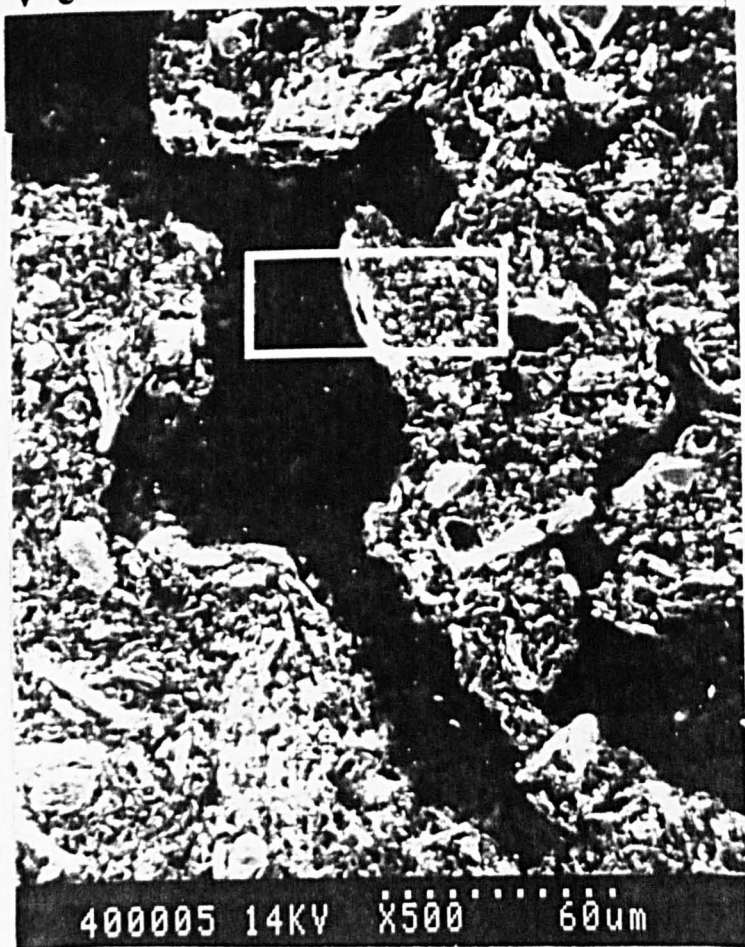
V a



V b

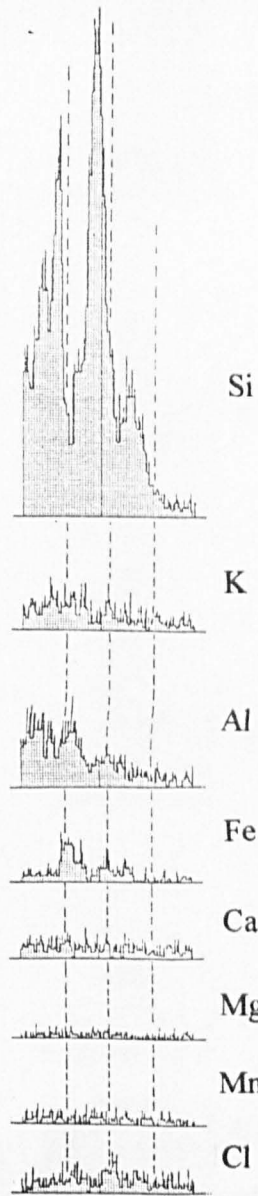
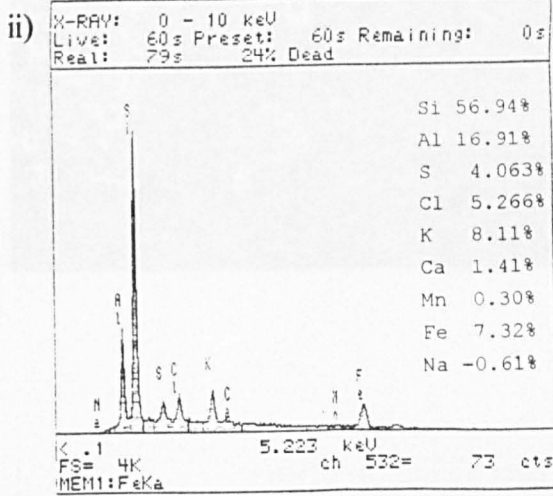
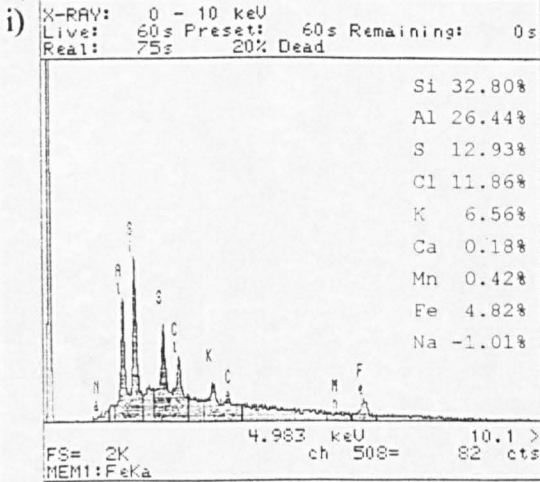


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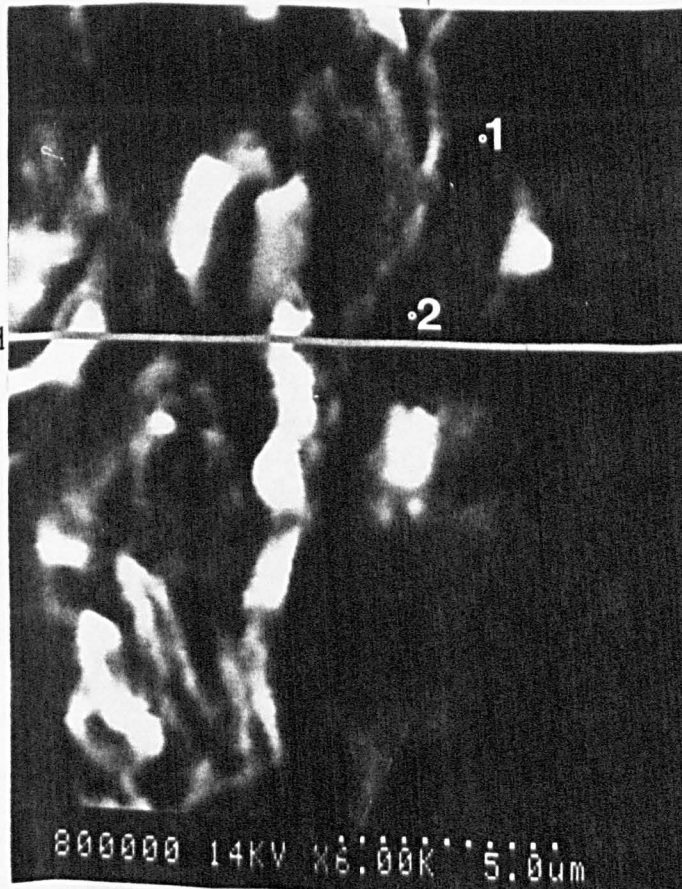


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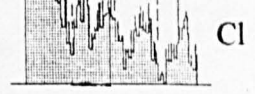
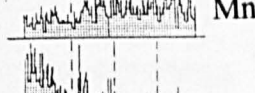
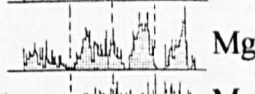
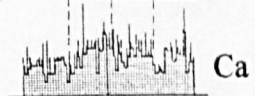
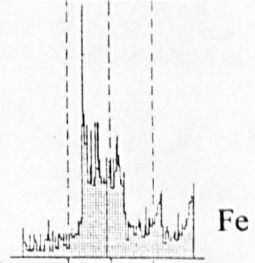
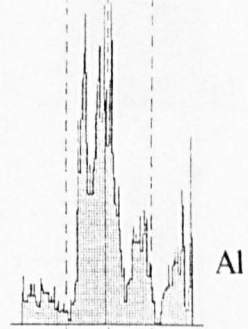
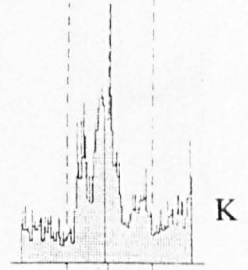
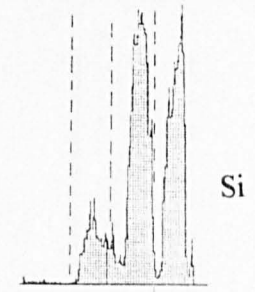
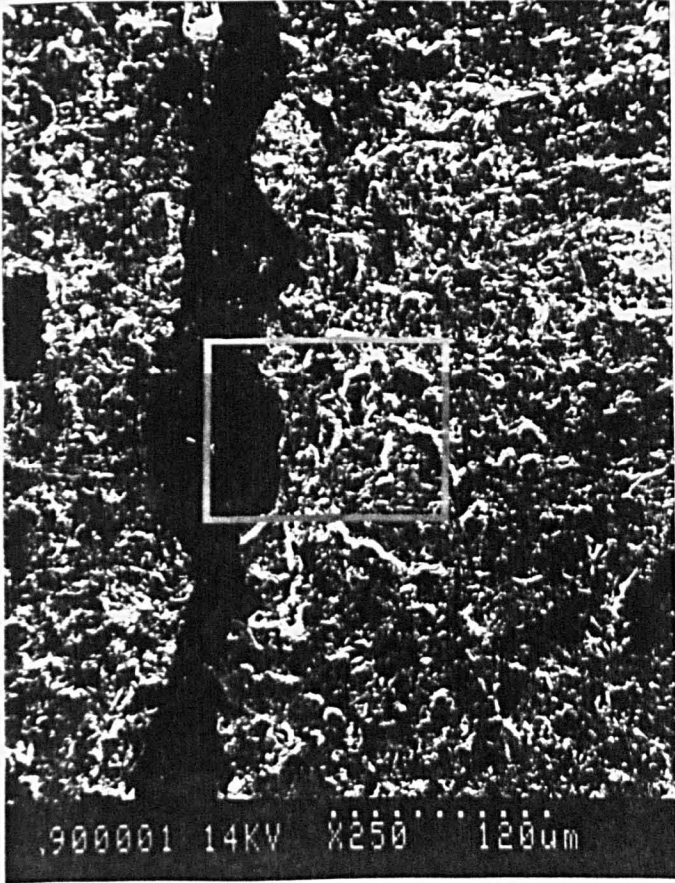
Spot scans



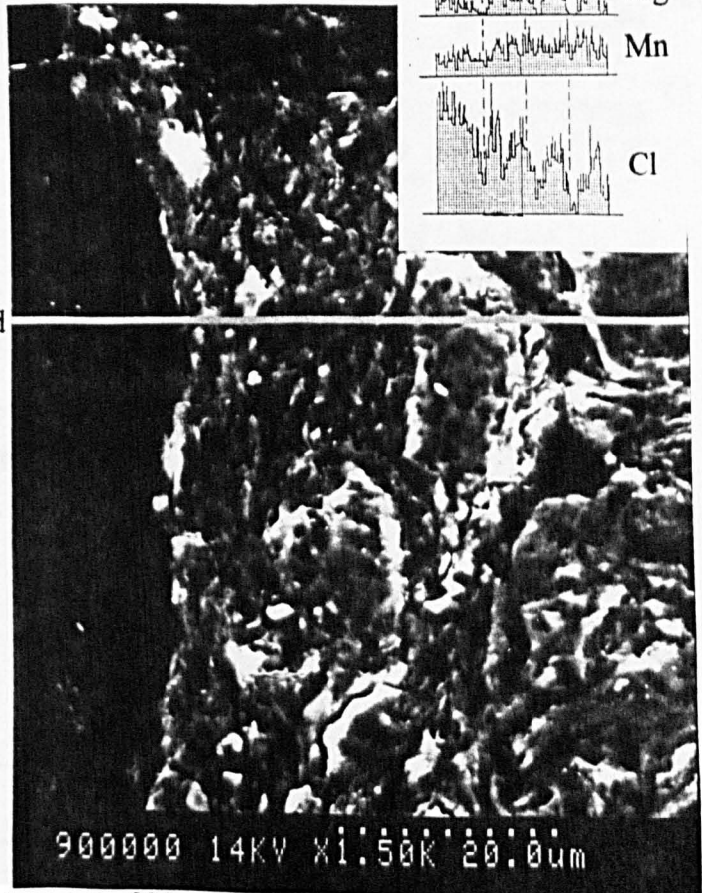
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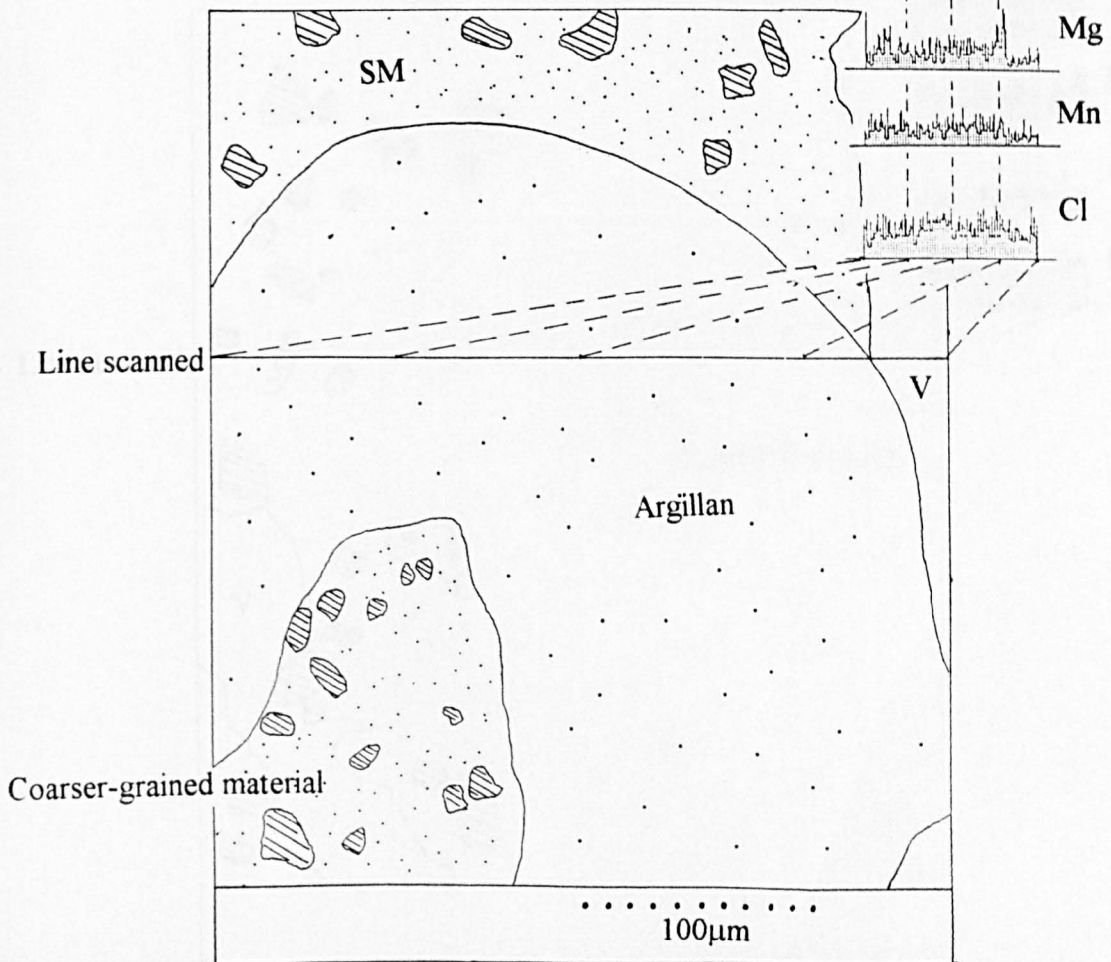
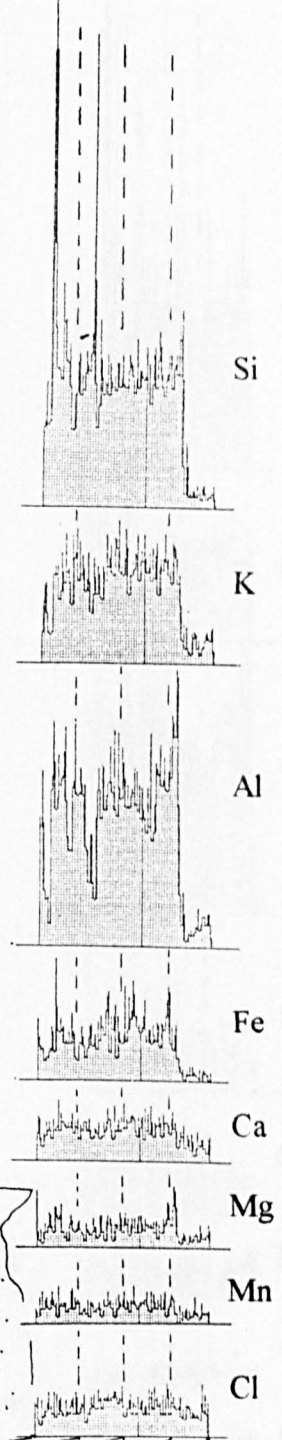
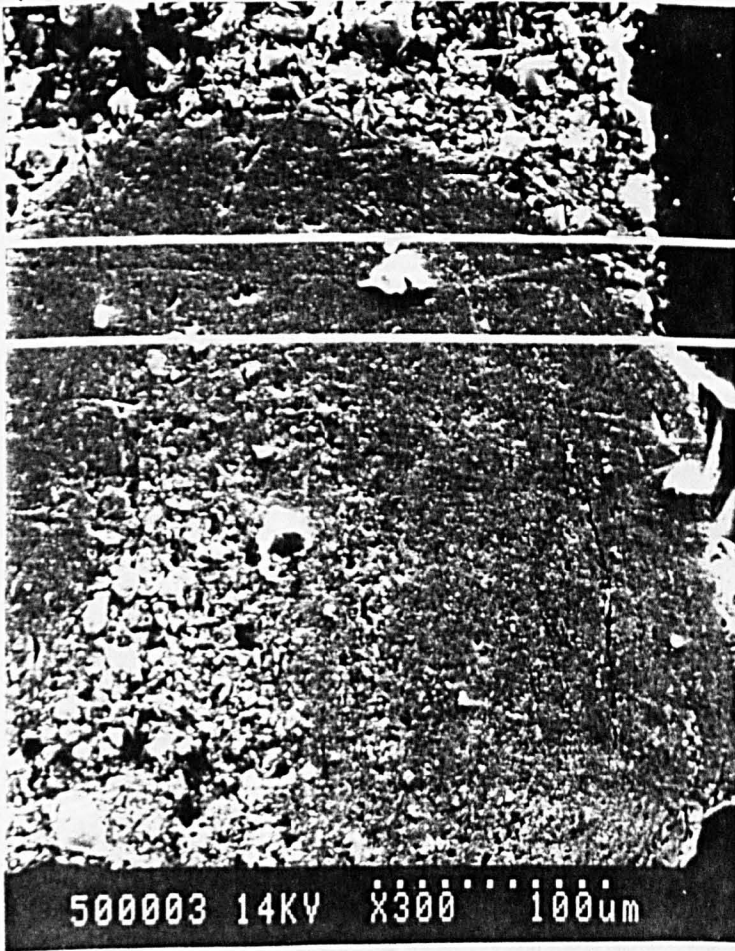
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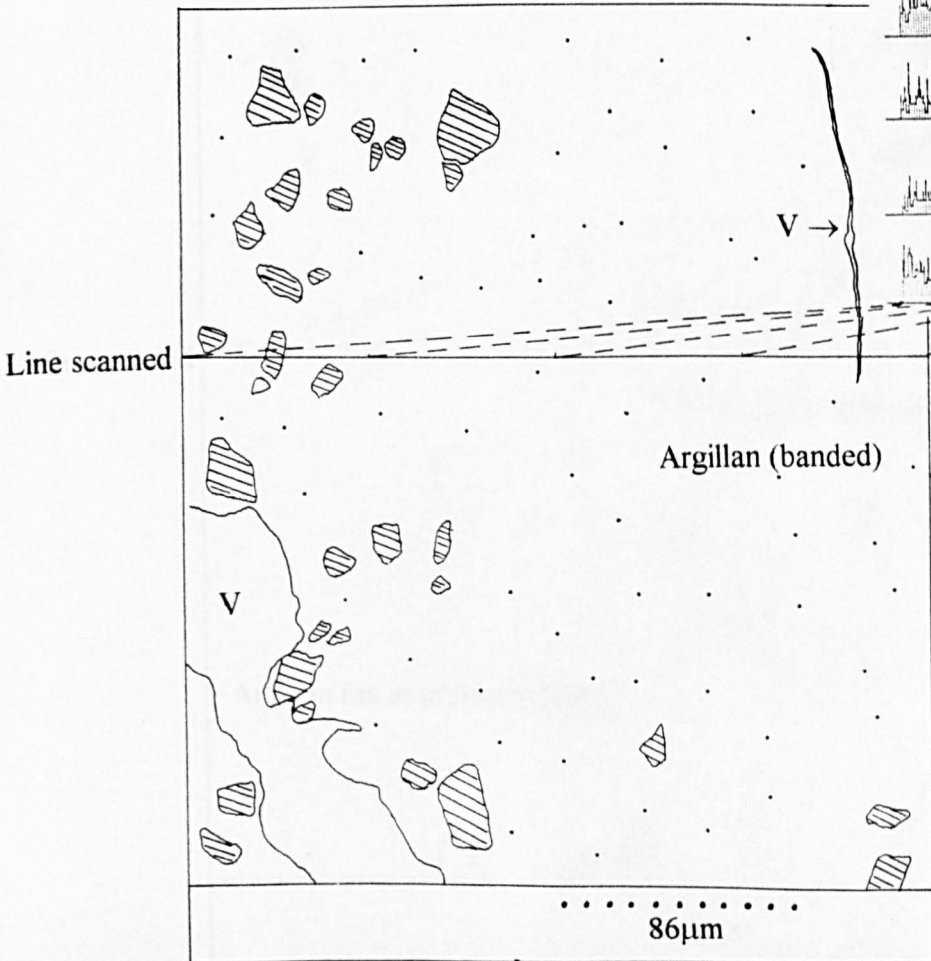
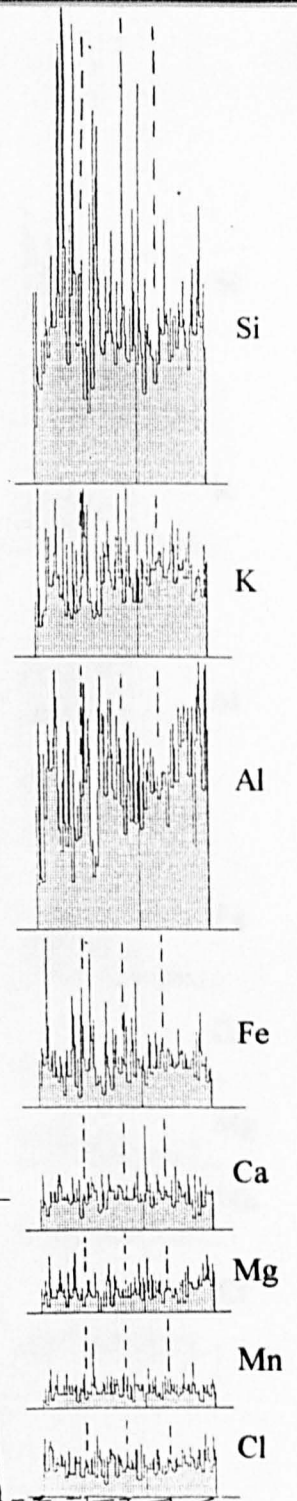
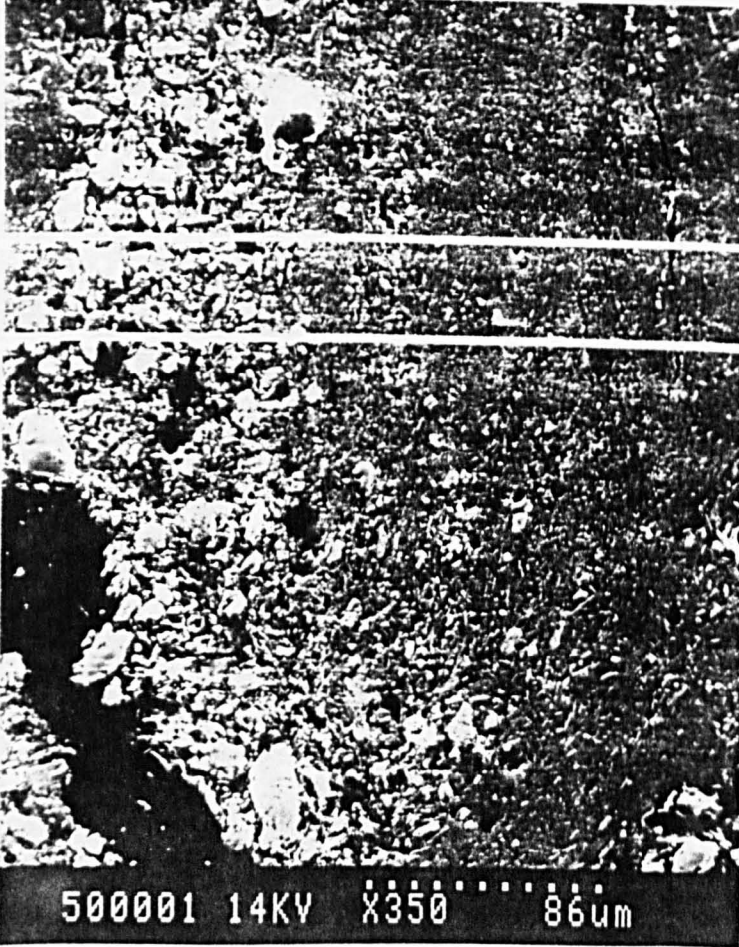
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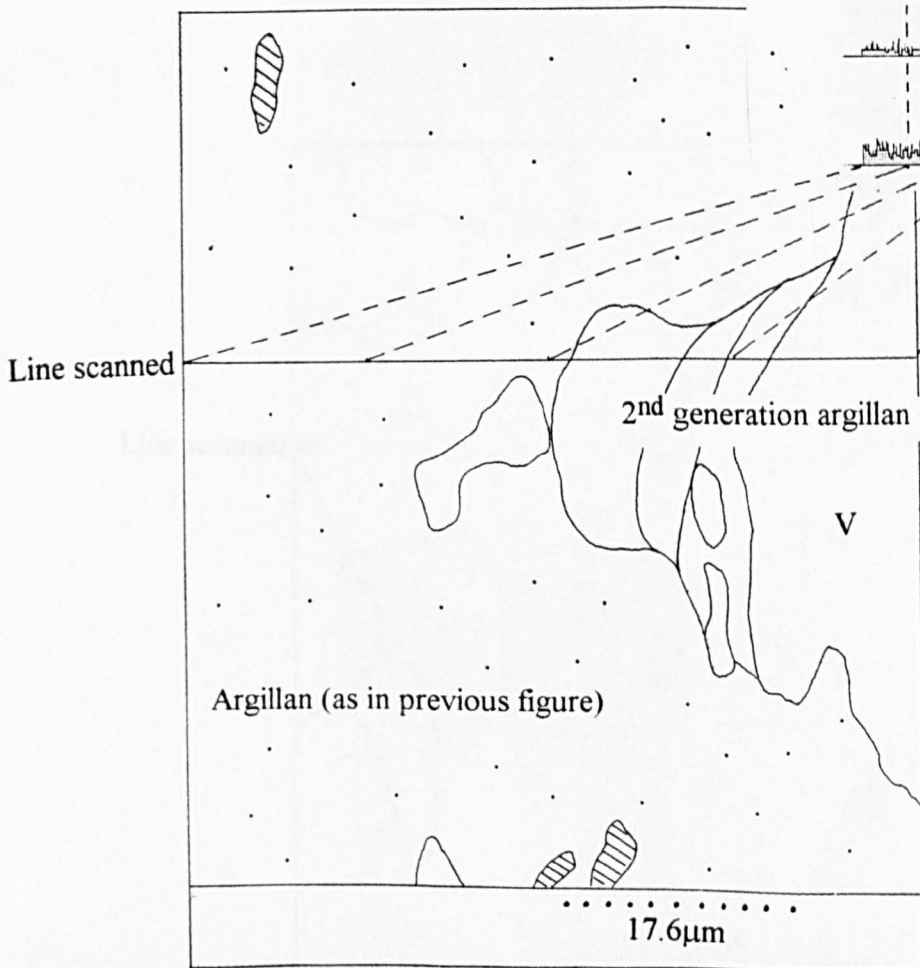
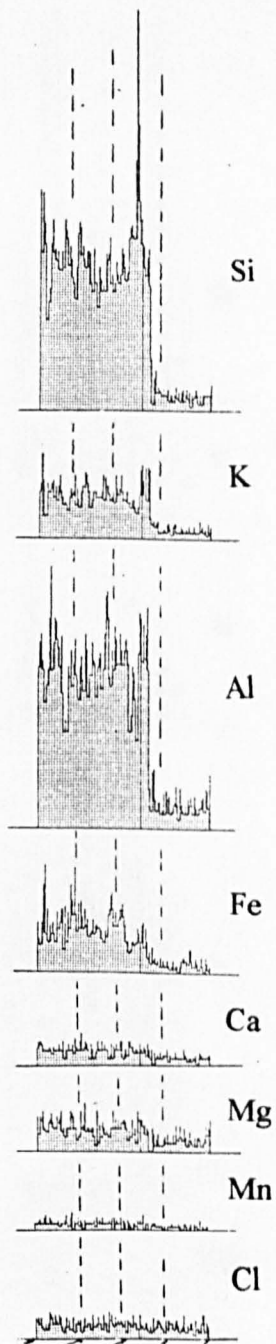
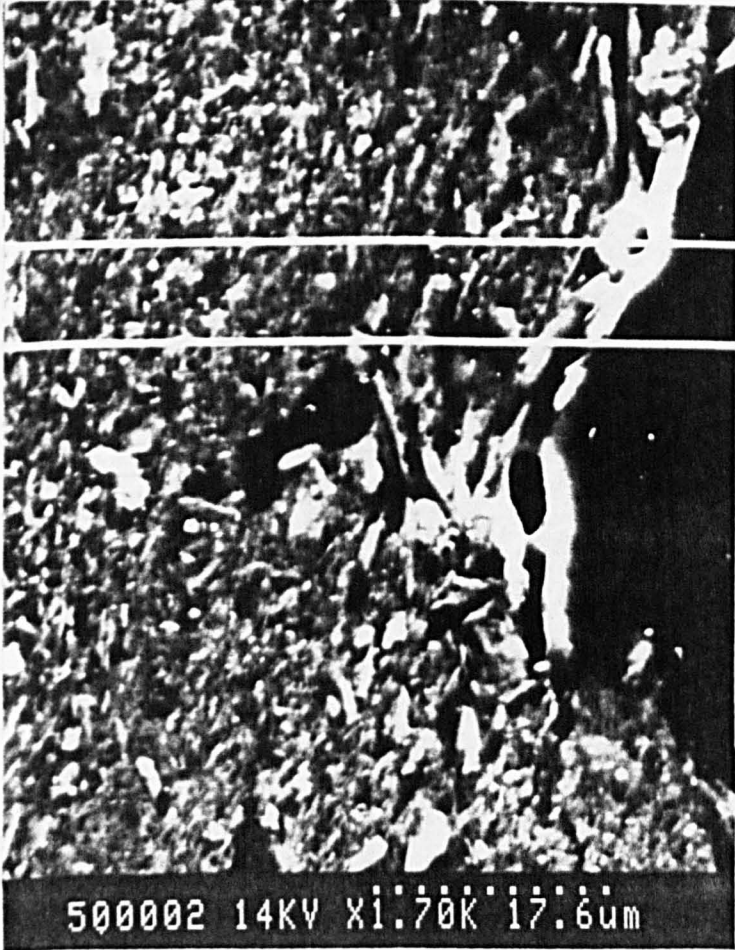
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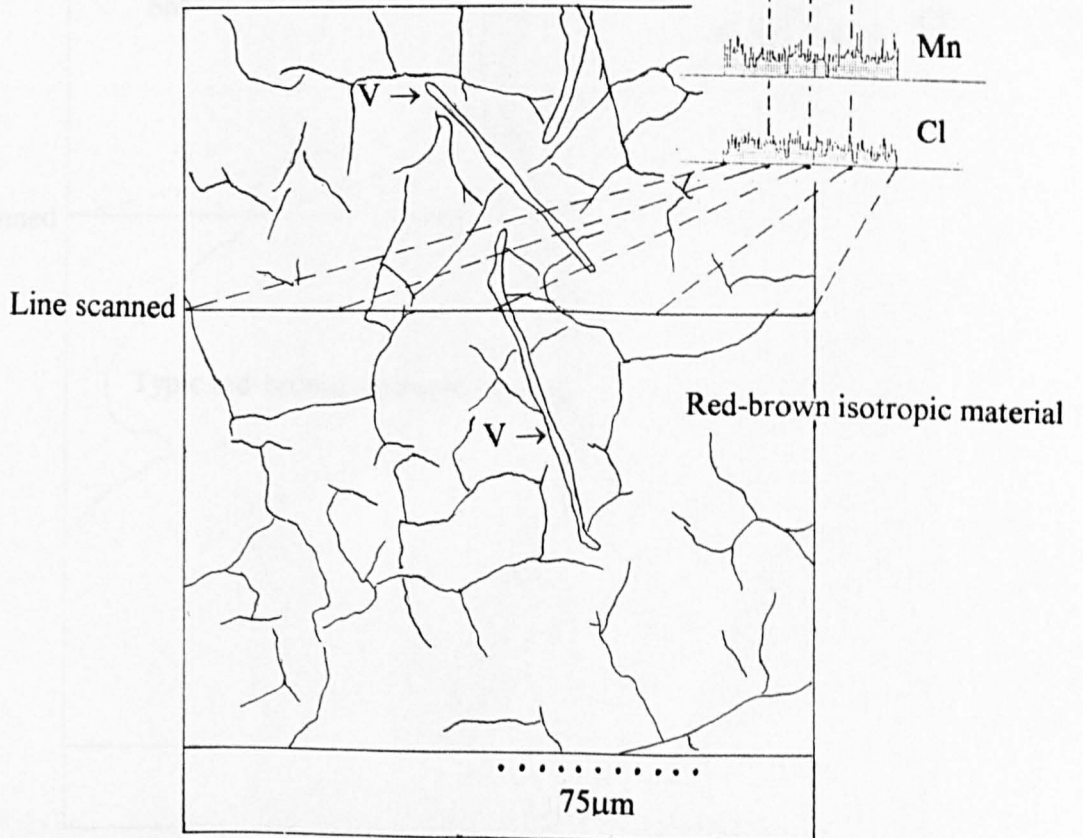
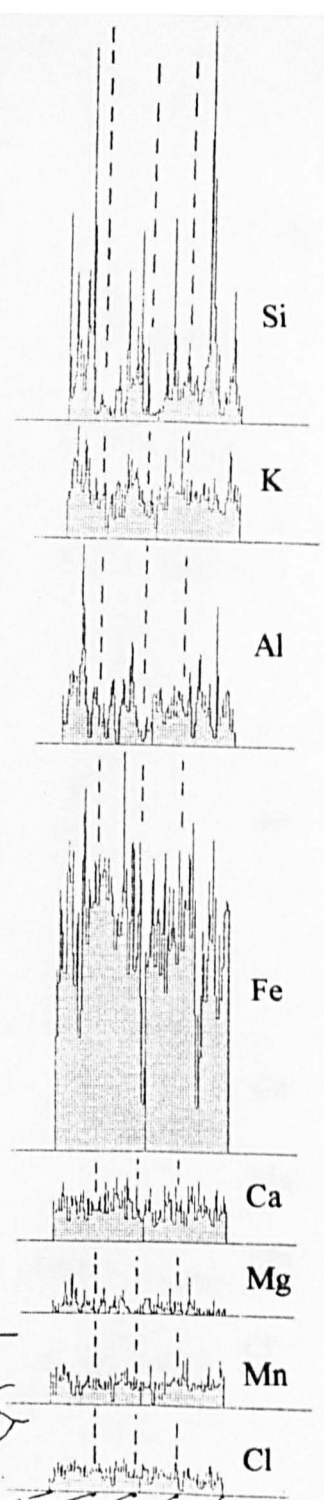
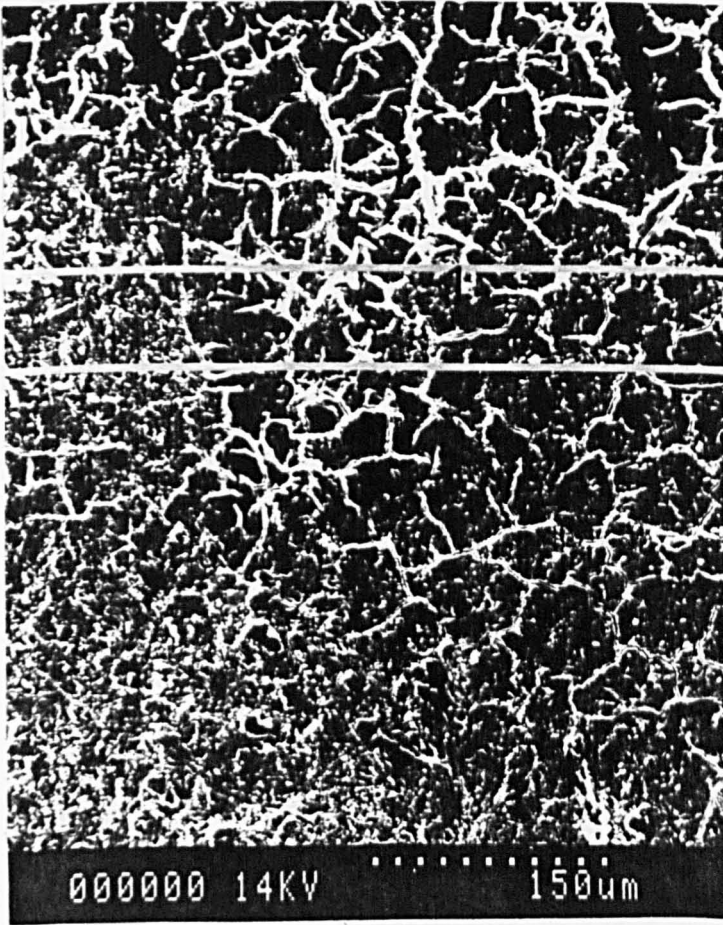
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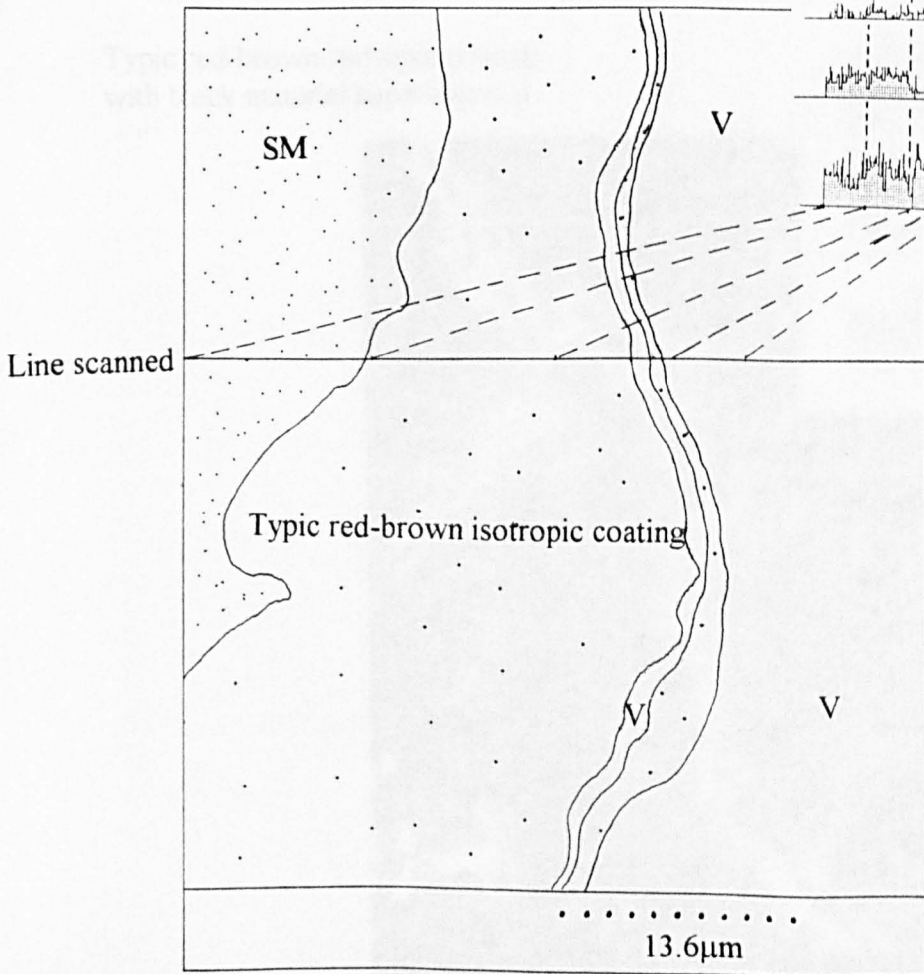
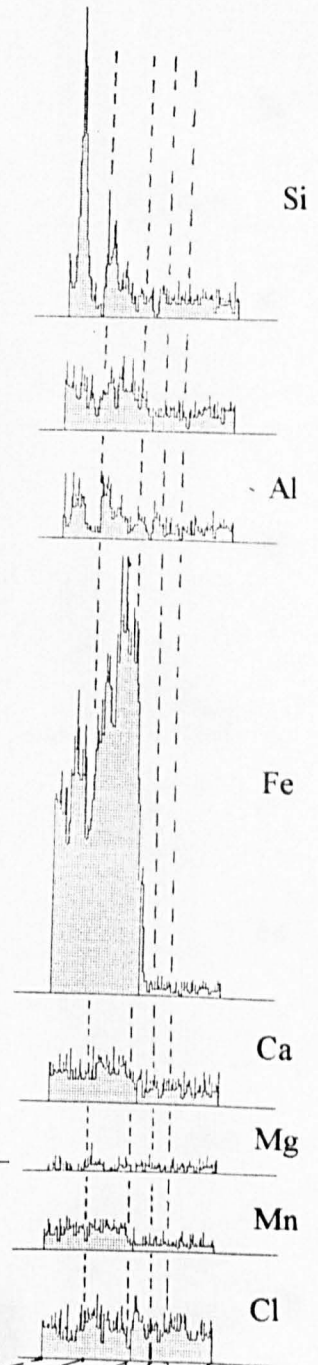
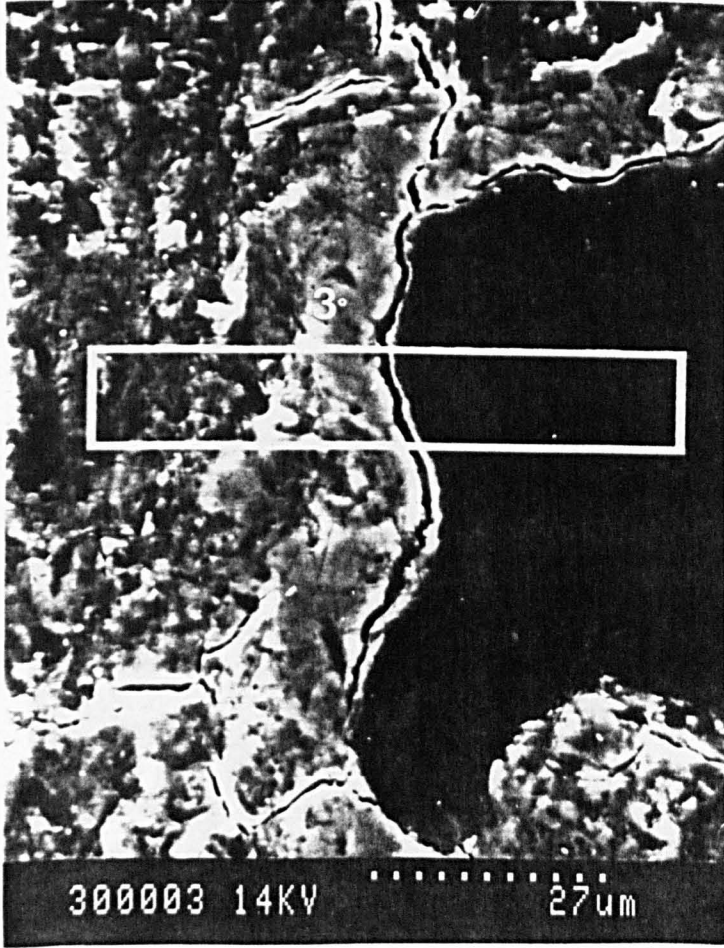
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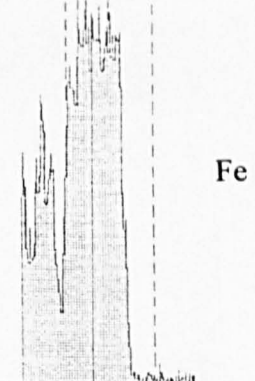
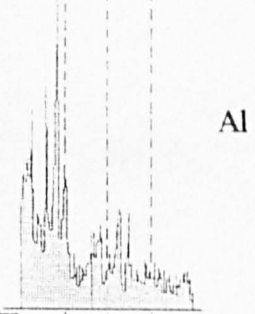
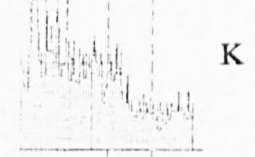
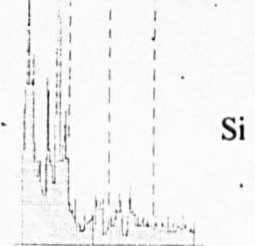
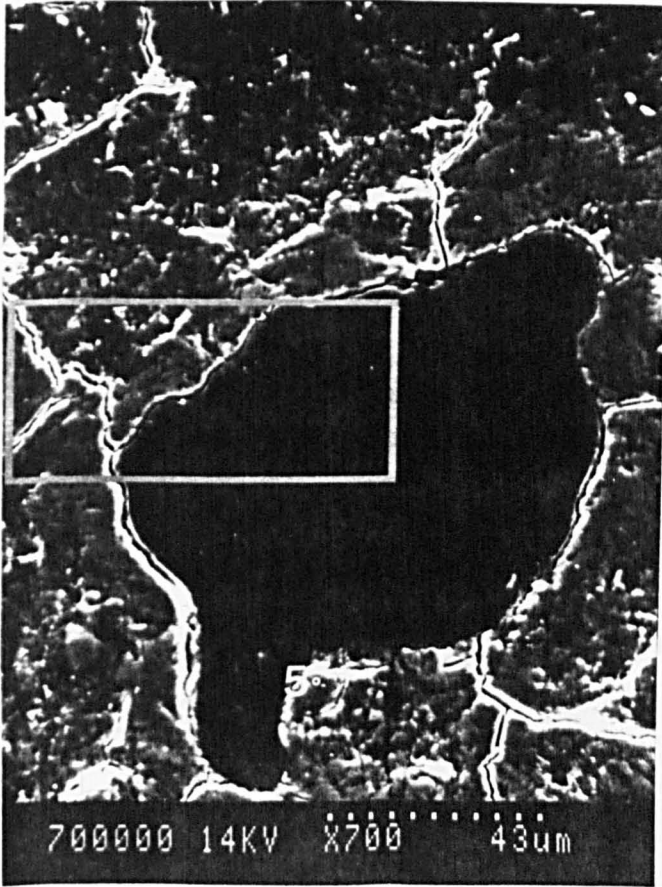
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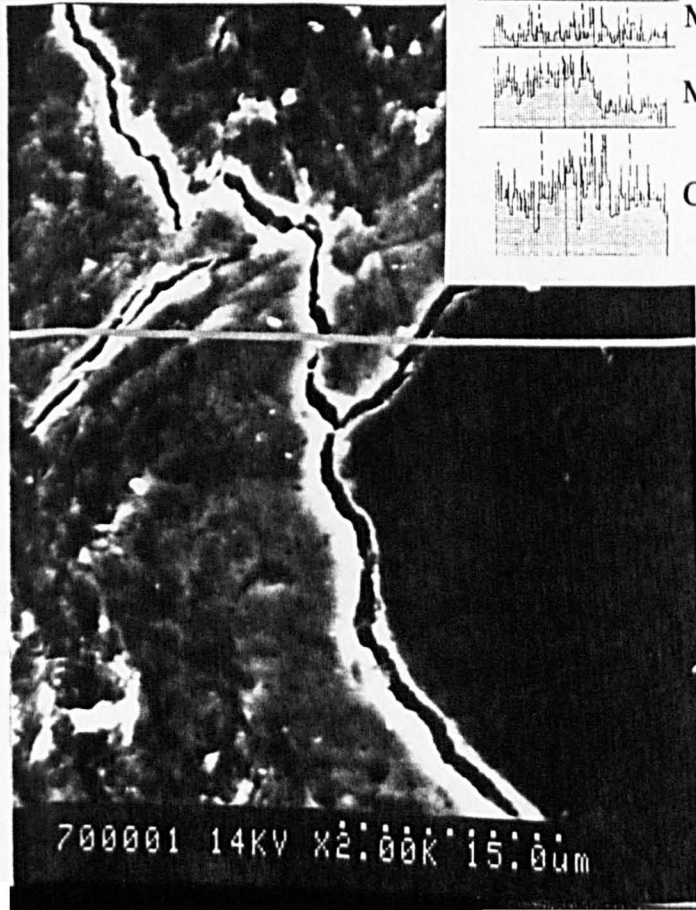
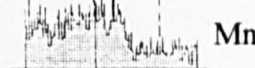
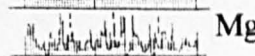
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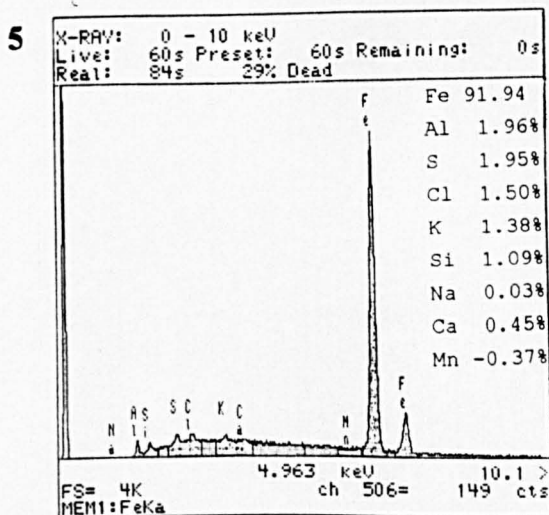
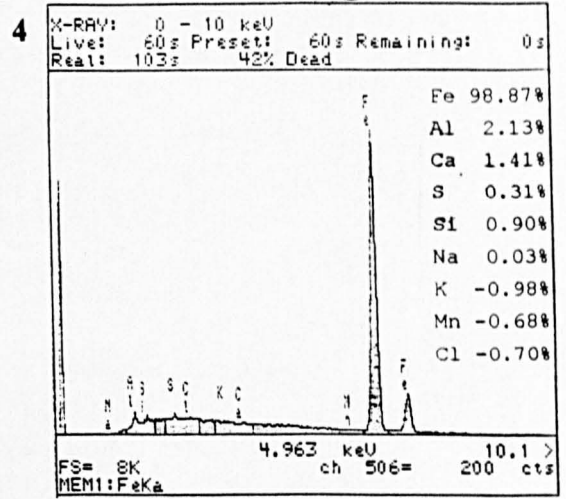
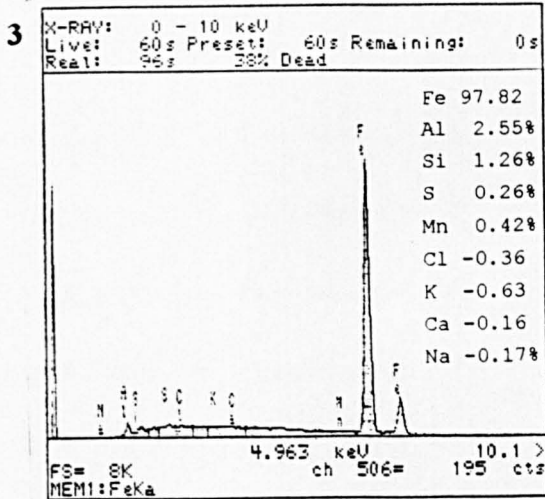
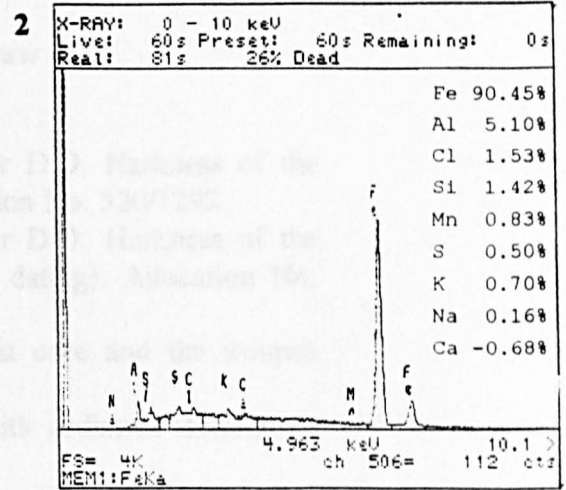
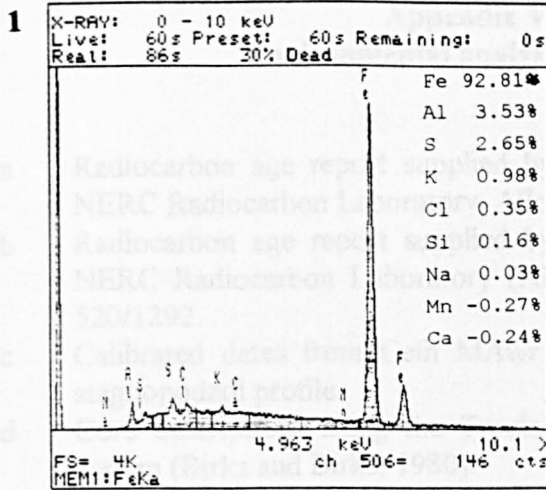


V k



Typic red-brown isotropic coating with black material superimposed





Appendix VI
Environmental analyses raw data

- a Radiocarbon age report supplied by Dr D.D. Harkness of the NERC Radiocarbon Laboratory. Allocation No. 520/1292.
- b Radiocarbon age report supplied by Dr D.D. Harkness of the NERC Radiocarbon Laboratory (AMS dating). Allocation No. 520/1292.
- c Calibrated dates from Cefn MAwr peat core and the ironpan stagnopodzol profile.
- d Core descriptions using the Troels-Smith sediment description system (Birks and Birks, 1980).
- e Macrofossil analysis of the Cefn Mawr core.
- f Macrofossil analysis of the Llyn y Foel-frech core.

**Appendix VIa Radiocarbon age report supplied by Dr. D.D. Harkness of the
NERC Radiocarbon Laboratory.**

Allocation No. 520/1292.

Cefn Mawr, Wales.

Organic detritus in sediment cored from small soligenous bog, Cefn Mawr, 0.7km SW of Llyn Aled Sailing Club, Hiraethog Moors, Clwyd, Wales (53° 6'N, 3° 38'W, Nat. Grid Ref. SH90755727). Core (5cm diam.) taken with Russian corer and quoted depth increments (in cm) relate to present bog surface. Coll. 1992 by J. Scourse, B. Lascelles and A. Nield subm. by D.A. Jenkins and J. Scourse, Univ. of Wales.

Prior to ¹⁴C measurement the raw samples were digested in 2M HCl (at 80°C for 24 hours, washed free of mineral acid and dried to constant weight.

SRR-5047	Cefn Mawr No. 10	48 - 51cm	395±45 δ ¹³ C = -26.5‰
SRR-5048	Cefn Mawr No. 9	72 - 75cm	580±50 δ ¹³ C = -27.4‰
SRR-5049	Cefn Mawr No. 8	217 - 220cm	2445±50 δ ¹³ C = -27.9‰
SRR-5050	Cefn Mawr No. 7	231 - 233cm	2805±50 δ ¹³ C = -27.9‰
SRR-5051	Cefn Mawr No. 6	255 - 258cm	3515±50 δ ¹³ C = -27.8‰
SRR-5052	Cefn Mawr No. 5	264 - 267cm	3530±55 δ ¹³ C = -27.9‰
SRR-5053	Cefn Mawr No. 4	293 - 296cm	4075±55 δ ¹³ C = -28.7‰
SRR-5054	Cefn Mawr No. 3	311 - 314cm	4475±50 δ ¹³ C = -30.0‰
SRR-5055	Cefn Mawr No. 2	374 - 377cm	4520±50 δ ¹³ C = -29.1‰
SRR-5056	Cefn Mawr No. 1	399 - 402cm	6175±50 δ ¹³ C = -29.4‰

**Appendix VIb Radiocarbon age report supplied by Dr. D.D. Harkness of the
NERC Radiocarbon Laboratory (AMS dating).**

Allocation No. 520/1292.

Publication code	RCL Target prep ref	Sample No. (Description)	Measured age (^{14}C years BP $\pm 1\sigma$)	% Modern carbon ($\pm 1\sigma$)	$\delta^{13}\text{C}_{\text{PDB}} \pm 0.1\text{‰}$	wt% carbon
AA15209	AMS/820	H1 Bf whole soil	1585 ± 50	82.09 ± 0.48	-26.8	6.8
AA15210	AMS/821	H2 Bf whole soil	1955 ± 50	78.39 ± 0.47	-26.8	5.6
AA15211	AMS/822	H2 Bf 0.1M pyrophosphate residue	1930 ± 50	78.64 ± 0.47	-26.3	-
AA15212	AMS/823	H2 Bf 5M HCl residue	1315 ± 50	84.90 ± 0.55	-28.1	-
AA15213	AMS/824	H3 charcoal	7365 ± 65	39.97 ± 0.31	-28.1	46.9
AA15214	AMS/825	H4 Of layer	1265 ± 60	85.44 ± 0.64	-28.3	26.7

Sampling location:

Samples were collected (May 1995) by D.B. Lascelles from freshly exposed soil profiles (2 and 3) on shoreline of Aled Isaf reservoir, Hiraethog Moors, Clwyd, Wales (53°7'N 33°9'W, Natl Grid Ref SH 914594 (profile A) and SH 915596 (profile B).

Sample composition:

Sample 1 and 2 are ironpan (Bf horizon) in profiles A and B respectively. Sample 3 is charcoal fragments recovered from the Bs horizon under the ironpan in profile B and sample 4 is peat from the base of the overlying Oh layer.

Sample context:

Individual samples were selected to test previous interpretations (Jenkins, 1991) of the development of ironpan stagnopodzols which are relatively widespread features in the soils of upland Britain. Particular emphasis was placed on specific organic fractions within the ironpan layer in an attempt to identify the older organic residues likely to record the best approximation to the timing of ironpan formation.

Samples Pretreatment:

Raw samples of the Bf soil were cleaned by physical removal of suspect rootlet material and adhering fragments of the Bs material under a x20 magnification. The soil was then oven dried at 105°C and ground in an agate mortar. An aliquot was taken to represent the "whole soil" and the remainder passed for pretreatment designed to chemically differentiate the "older" from the "younger" residues.

Pyrophosphate extraction: 0.5g of soil was refluxed in 50ml sodium pyrophosphate for 10 hours at 80°C. The solid residue was recovered by filtration, washed with distilled water and dried to constant weight in a vacuum oven.

Hydrochloric acid extraction: 0.5g of soil was refluxed in 20ml of 6M HCl for 10 hours at 80°C. The solid residue was recovered by filtration, washed with distilled water and dried to constant weight in a vacuum oven.

Charcoal fragments (sample 3) were subjected to successive digestions in 2M potassium hydroxide (at 80°C) until the supernatant showed no colouration due to extracted humic material. The alkali insoluble residue was allowed to stand overnight in hot 0.5M hydrochloric acid then washed to neutral pH and oven dried at 105°C. Peat from the Oh horizon (sample 4) was digested overnight at 80°C in 2M hydrochloric acid and then washed free from mineral acid and dried to constant weight.

Appendix VIc Calibrated dates from Cefn Mawr peat core and ironpan stagnopodzolic soil

See over.

Uncalibrated date (¹⁴ C years BP)	Ref number	Calibrated ages						Cal AD/BC ranges from probability distribution		
		Cal. age (BP)		Minimum of cal. age ranges		Maximum of cal. age ranges		% area included	cal AD (cal BP) age ranges	Relative area under probability distribution
		1σ	2σ	1σ	2σ	1σ	2σ			
395±45	SRR-5047	AD1464 BP486	AD1464 BP486	AD1442 BP508	AD1428 BP522	AD1510 BP440	AD1635 BP315	68.3	AD1439-1514 (511-436)	0.87
								95.4	AD1600-1616 (350-334)	0.13
580±50	SRR-5048	AD1328, 1333,1395 (622,617, 555)	AD1328, 1333,1395 (622,617, 555)	AD1300 BP650	AD1280 BP670	AD1410 BP540	AD1430 BP520	68.3	AD1428-1550 (522-400)	1.00
								95.4	AD1306-1359 (644-591)	0.66
									AD1379-1407 (571-543)	0.34
									AD1288-1421 (662-529)	
2445±50	SRR-5049	BC751,721,5 26 (2700,2670,2 475)	BC751,721,5 26 (2700,2670, 2475)	BC764 BP2713	BC790 BP2739	BC407 BP2356	BC400 BP2349	68.3	BC759-684 (2708-2633)	0.35
								95.4	BC656-640 (2605-2589)	0.07
									BC549-411 (2498-2360)	0.58
									BC765-671 (2714-2620)	0.29
									BC668-611 (2617-2560)	0.14
									BC607-406 (2556-2355)	0.56
2805±50	SRR-5050	BC980,960,9 38 (2929,2909,2 887)	BC980,960,9 38 (2929,2909, 2887)	BC1014 BP2963	BC1100 BP3049	BC907 BP2856	BC840 BP2789	68.3	BC1021-905 (2970-2854)	1.00
								95.4	BC1097-839 (3046-2788)	1.00
3515±50	SRR-5051	BC1882 BP3831	BC1882 BP3831	BC1917 BP3866	BC2017 BP3966	BC1767 BP3716	BC1708 BP3657	68.3	BC1916-1858 (3865-3807)	0.40
								95.4	BC1848-1768 (3797-3717)	0.60
									BC2019-2001 (3968-3950)	0.02
									BC1981-1736 (3930-3685)	0.97
3530±55	SRR-5052	BC1886 BP3835	BC1886 BP3835	BC1943 BP3892	BC2030 BP3979	BC1774 BP3723	BC1740 BP3689	68.3	BC1947-1865 (3896-3814)	0.53
								95.4	BC1846-1772 (3795-3721)	0.47
									BC2033-1738 (3982-3687)	1.00
4075±55	SRR-5053	BC2651, 2649,2610 (4600,4598,4 559)	BC2651, 2649,2610 (4600,4598, 4559)	BC2863 BP4812	BC2878 BP4827	BC2505 BP4454	BC2470 BP4419	68.3	BC2862-2814 (4811-4763)	0.27
									BC2736-2728 (4685-4677)	0.04
									BC2695-2680 (4644-4629)	0.07
									BC2665-2631 (4614-4580)	0.18
									BC2629-2573 (4578-4522)	0.31
									BC2534-2507 (4483-4456)	0.12
								95.4	BC2874-2802 (4823-4751)	0.24
									BC2764-2716 (4713-4665)	0.10
									BC2705-2489 (4654-4438)	0.66

Uncalibrated date (¹⁴ C years BP)	Ref number	Calibrated ages						Cal AD/BC ranges from probability distribution		
		Cal. age (BP)		Minimum of cal. age ranges		Maximum of cal. age ranges		% area included	cal AD (cal BP) age ranges	Relative area under probability distribution
		1σ	2σ	1σ	2σ	1σ	2σ			
4475±50	SRR-5054	BC3292, 3274,3269, 3244,3103 (5241,5223, 5218,5193, 5052)	BC3292, 3274,3269, 3244,3103 (5241,5223,5 218,5193, 5052)	BC3334 BP5283	BC3350 BP5299	BC3040 BP4989	BC2928 BP4877	98.3	BC3330-3227 (5279-5176)	0.51
								95.4	BC3185-3156 (5134-5105) BC3143-3091 (5092-5040) BC3064-3043 (5013-4992) BC3346-3030 (5295-4979) BC2976-2936 (4925-4885)	0.14 0.25 0.10 0.95 0.05
4520±50	SRR-5056	BC3331, 3226,3185, 3155,3143 (5280,5175, 5134,5104, 5092)	BC3331, 3226,3185, 3155,3143 (5280,5175,5 134,5104, 5092)	BC3349 BP5298	BC3370 BP5319	BC3101 BP5050	BC3040 BP4989	68.3	BC3343-3298 (5292-5247) BC3241-3171 (5190-5120) BC3169-3105 (5118-5054)	0.25 0.39 0.35
								95.4	BC3367-3082 (5316-5031) BC3067-3042 (5016-4991)	0.96 0.04
6175±50	SRR-5057	BC5206, 5151,5150 (7155,7100, 7099)	BC5206, 5151,5150 (7155,7100,7 099)	BC5230 BP7179	BC5240 BP7189	BC5063 BP7012	BC4947 BP6896	68.3	BC5227-5195 (7176-7144) BC5180-5131 (7129-7080) BC5125-5067 (7074-7016)	0.23 0.36 0.40
								95.4	BC5242-4995 (7191-6944) BC4971-4947 (6920-6896) AD422-533 (1528-1417)	0.97 0.02 1.00
1585±50	AA15209 AMS/820	AD438 BP1512	AD438 BP1512	AD413 BP1537	AD348 BP1602	AD542 BP1408	AD600 BP1350	68.3	AD375-595 (1575-1355)	0.99
1955±50	AA15210 AMS/821	AD54 BP1896	AD54 BP1896	BC6 BP1955	BC90 BP2039	AD85 BP1865	AD130 BP1820	68.3	BC26-AD89 (1975-1861)	1.00
								95.4	BC96-AD135 (2045-1815)	1.00
1930±50	AA15211 AMS/822	AD72 BP1878	AD72 BP1878	AD14 BP1936	BC40 BP1989	AD119 BP1831	AD203 BP1747	68.3	AD12-120 (1938-1830)	1.00
								95.4	BC47-AD212 (1996-1738)	1.00
1315±50	AA15212 AMS/823	AD675 BP1275	AD675 BP1275	AD658 BP1292	AD640 BP1310	AD763 BP1187	AD790 BP1160	68.3	AD658-722 (1292-1228) AD738-763 (1212-1187)	0.75 0.25
								95.4	AD630-817 (1320-1133)	0.99
7365±65	AA15213 AMS/824	BC6175 BP8124	BC6175 BP8124	BC6232 BP8181	BC6410 BP8359	BC6109 BP8058	BC6080 BP8029	68.3	BC6368-6329 (8317-8278) BC6234-6106 (8183-8055)	0.18 0.82
								95.4	BC6405-6083 (8354-8032)	1.00
1265±60	AA15214 AMS/825	AD720,739, 761 (1230,1211, 1189)	AD720,739, 761 (1230,1211,1 189)	AD671 BP1279	AD650 BP1300	AD801 BP1149	AD890 BP1060	68.3	AD671-800 (1279-1150)	1.00
								95.4	AD658-885 (1292-1065)	1.00

**Appendix VI d Core descriptions using the Troels-Smith sediment description system
(Birks and Birks, 1980)**

Cefn Mawr

Depth (cm)	nig	strf	elas	sicc	humo	Colour	Boundary	Composition
0-13	3	0	3	2	2	brown	v. gradual	Tb1, Th2, Dh1
13-60	3	0	3	2	2	brown	gradual	Tb+, Th3, Dh1
60-125	4	0	3	2	3	black	v. gradual	Sh1, Th2, Dh1
125-170	4	0	3	2	4	black	gradual	Sh2, Th2
170-230	4	0	3	2	4	black	v. gradual	Sh3, Th1
230-257	4	0	1	2	4	black	gradual	Sh4
257-395	4	0	1	2	4	black	gradual	Sh3, Dl1
395-403	3	0	1	2	4	dark brown	gradual	Sh3, Ag1
403-425	1	1	1	3	1	grey	sharp	Ag3, Sh1

Llyn y Foel-frech

Depth (cm)	nig	strf	elas	sicc	humo	Colour	Boundary	Composition
0-30	-	-	-	1	-	black	gradual	-
30-100	4	0	2	3	4	black	gradual	Ld4, Dg+
100-217	3	0	1	3	4	dark brown	sharp	Ld3, Dl1
217-330	2	0	0	3	4	grey	gradual	Ag4
330-342	1	0	0	3	3	light grey	gradual	Ag4

Key:

nig = nigror (the degree of darkness)
 strf = stratificatio (the degree of stratification)
 elas = elasticitas (the degree of elasticity)
 sicc = siccitas (the degree of dryness)
 humo = humositas (the degree of humification)

Scale:

0 = absent
 1 = up to ¼
 2 = ¼ to ½
 3 = ½ to ¾
 4 = whole
 + = trace, less than one eight

Sh = Substantia humosa (humous substance)

Tb = Turfa bryophytica (moss peat)

Th = Turfa herbacea (herbaceous peat)

Dl = Detritus lignosus (fragments of wood and bark >2mm in size)

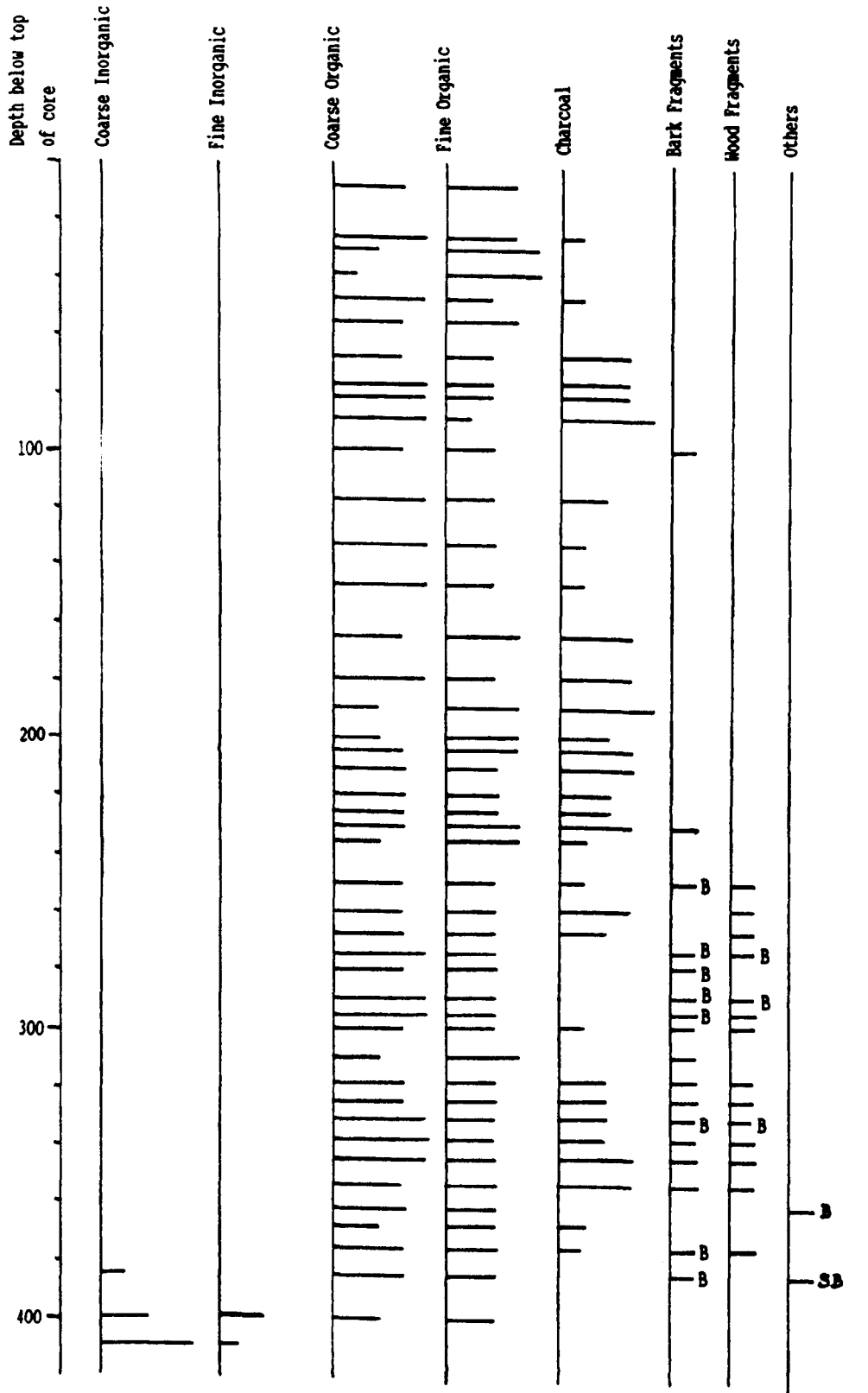
Dh = Detritus herbosus (fragments of herbaceous plants >2mm in size)

Dg = Detritus granosus (fragments of woody and herbaceous plants <2mm in size)

Ag = Argilla granosa (silt composed of mineral particles between 0.06 and 0.002mm in size).

Ld = Limus detrituosus (lake mud)

Appendix Ve Macrofossil analysis of the <118m fraction of the Cefn Mawr core



Line denotes presence

Rare
 Occasional
 Frequent
 Abundant

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B=Betula
 SB=Betula Seed
 L=Betula leaf
 S=Unidentified seed

Appendic Vf Macrofossil analysis of the <118m fraction of the Llyn y Foel-frech core

