GEOCHEMICAL AND PALYNOCOLOGICAL SIGNALS FOR PALAEOENVIRONMENTAL
CHANGE IN SOUTH WEST ENGLAND

by

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A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

DOCTOR OF PHILOSOPHY

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July 1997.
ABSTRACT

This thesis evaluates the utility of a geochemical technique for the investigation of palaeoenvironmental change in south west England. The method, EDMA (Energy Dispersive X-ray Micro Analysis), is a rapid, non-destructive analysis tool, capable of detecting a large range of geochemical elements.

This research examines the most appropriate method of sample preparation for organic soils and peats, and investigates the reliability of results gained from EDMA with respect to conventional bulk geochemical techniques. A detailed study focused on a range of different sedimentary sites in south west England where a variety of palaeoenvironmental changes were thought to occur. Pollen analysis was undertaken on the same sedimentary material, and provided complementary information on the nature and scale of vegetation change through time. Sediments from a coastal valley mire near North Sands, Salcombe, revealed information relating to the processes of sea-level change in this part of south Devon and the subsequent autogenic processes as the sediment accumulated through time. A range of sites were located on the granitic upland of Dartmoor. A raised bog, Tor Royal, provided data relating to the changing nature of the central upland landscape from late Mesolithic times to the present day. Two soligenous sites, Upper Merrivale and Files Copse, sought to investigate the activities of postulated anthropogenic activity at a much smaller spatial scale, with particular interest placed upon the evidence for deforestation activity and the utilisation of the local mineral resources. The last site, Crift Down, a lowland spring fed valley mire utilised geochemical and palynological fluxes within the peat to investigate processes and activities associated with archaeological evidence for Medieval tinworking in this area of Cornwall.

The results from the EDMA investigations, and comparable studies using other geochemical methods including EMMA, AAS and flame photometry, suggest the technique to have greatest applicability as a first stage tool in the analysis of general activities of past environmental change. The technique was found to yield reliable results for the major elements (Si, Al, S, Fe, Ca, K, Na and Mg), but is generally incapable of providing useful data on heavy metal elements.

The data from south west England suggest the method to reflect activity at a range of different scales, and as part of a structured programme of analysis may contribute information to allow a more holistic environmental reconstruction to be made.
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Acknowledgements

I firstly wish to acknowledge the Department of Geographical Sciences, University of Plymouth for the internal grant from HEFCE funds which made this study possible. Great thanks are due to the project supervisors, Dr. Dan Charman and Dr. John Grattan, for their encouragement, comment and friendship. Thanks also to the technical staff of the University of Plymouth for their time and knowledgeable guidance, including Dr. Roy Moate, Brian Lakey and Jane Green of the EM unit; Alexandra Fraser of the Department of Environmental Science for carrying out the AAS work on the North Sands sediment; Ann Kelly, Kevin Solman, Pat Bloomfield and Richard Hartley of the Department of Geographical Sciences for considerable assistance throughout the fieldwork and laboratory components of this project. I owe a considerable debt of gratitude to my trusty band of field slaves: Dr. Ben Gearey, Richard Armitage, Carl Ishemo particularly after a broken scaphoid bone meant I merely ‘supervised’ the coring of Piles Copse.

I owe thanks to the Dartmoor National Park Authority, the Duchy of Cornwall, English Nature and South West Water for guidance with field sampling and permitting access to a number of the fieldsites, and Dr. Chris Caseldine of the Department of Geography, University of Exeter, and Dr. Tom Greeves for valuable comments. Thanks are due to NERC for the provision of three radiocarbon dates from Tor Royal in conjunction with another project. Thanks also to the landowners of the various sites, including Mrs. Mary Alford (Upper Merrivale), and Mr. Roger Howell (Piles Copse). Further thanks are extended to English Nature for permission to core in the environmentally sensitive locations at Tor Royal and Piles Copse, South West Water and Stephen Reed of Exeter Archaeological Field Unit for providing the North Sands sediment. Thanks to Dr. Gerry McDonnell of the Department of Archaeological Science, University of Bradford for detailed information on Crift Down, who with Mr. Eric Higgs and Phil Burton proved invaluable in the coring of this location. Thanks also to the Department of Geographical Sciences and Dr. Bill Shotyk of the Geological Institute, University of Berne for providing funds to enable me to present selected aspects of this research at an international workshop on peat bog archives of heavy metal deposition. Thanks are also due to Dr. Andrij Cheburkin of the Institute of Geological Sciences, Ukrainian Academy of Sciences, Kiev for providing the EMMA data.

Finally, I wish to thank the many people who have attempted to keep me sane (!) throughout the duration of this research project: the weekend combat drinking crew, Ben, Martin, Hoggy, Andy Collins, Mel, Andy Clegg, Teresa, Kim, Ollie, Grum, Piers and more recently, Ginger Jon, Gobber, Andy E., Karen, Mel G., Matt and Niall (aka the Fish Twins) and the lads from sunny Weston-super-Mare, Keith, Steve, Mike and my brother, Dave. I love you all.
AUTHOR'S DECLARATION

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

This study was financed with the aid of a studentship from the Higher Education Funding Council for England, through the Department of Geographical Sciences, University of Plymouth.

Publications:

*Published:*

*In press:*

Presentations and Conferences Attended:

April 1995. 'Geochemical and palynological signals for palaeoenvironmental change'. Postgraduate Palaeoecology Conference. Department of Geographical Sciences, University of Plymouth.


April 1996. 'Palaeoenvironments on Dartmoor: Merrivale and Tor Royal'. Postgraduate Palaeoecology Conference. Department of Zoology, University of Cambridge.

April 1996. 'Palaeoenvironmental investigations at Tor Royal, central Dartmoor'. Quaternary Research Association. Annual field meeting, Devon and East Cornwall.


Signed

Date 29.10.1997

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Chapter 1
Introduction

1.0 Introduction

This chapter begins with a discussion of the primary research aims. The history and development of Energy Dispersive X-Ray Micro Analysis (EDMA) as a research tool is discussed. A section is presented detailing the processes of X-ray production, detection and correction procedures. A short discussion presents the recent literature illustrating the uses of EDMA as a palaeoenvironmental tool. The final part considers the interpretational possibilities that may be gained from geochemical studies of peatland systems based on a review of published literature on the subject.

1.1 Research aims

The primary aim of this research project is to explore and develop a new technique for the reconstruction and interpretation of palaeoenvironmental change in south west England. The technique, EDMA, has been shown by preliminary studies (Grattan, 1994; Grattan et al., 1996) to have the capability of identifying a range of elements simultaneously (Goldstein et al., 1981; Lawes, 1987) from a variety of different sedimentary contexts. Grattan (1994) first applied EDMA to the analysis of Holocene palaeoenvironmental conditions in northern Scotland. However, he largely adopted the methodologies of Pyatt et al. (1991) and Pyatt and Lacy (1988) with respect to sample preparation and did not compare results with other techniques and did not critically evaluate the reliability of the data for different elements. This research project thus seeks to:

(i) investigate the capability of EDMA to produce meaningful geochemical results with respect to other geochemical methods,

(ii) evaluate the most appropriate sample preparation method for the sediments under investigation,

(iii) contribute to the palaeoenvironmental database for south west England through a series of case studies.

The research will apply EDMA, pollen and carbon analysis to a range of palaeoenvironmental situations representing different levels and types of past environmental change in south west England. Palynological investigations will be used both as a standard technique with which to compare results, and to provide complementary information on the detail and nature of the
environmental changes occurring.

A number of sites have been identified which will test the efficiency of the technique to provide meaningful palaeoenvironmental data from different sediment body types e.g. raised, valley and soligenous mire (section 2.2). These sites should also provide detailed information on natural environmental development (soil evolution, vegetation succession) and human induced changes arising from deforestation, cultivation and cultural changes in prehistory, the Medieval period and more recent times. Particular emphasis will be placed upon the detection of prehistoric and Medieval tinning activity in south west England and the associated effect this has upon peatland ecosystems.

EDMA together with pollen analysis will therefore extend our knowledge of environmental development of south west England from early Holocene times.

1.2 EDMA: a technique for palaeoenvironmental reconstruction

This section presents a brief outline to EDMA. It deals with the history of the technique from the early discoveries of the 1920s to the wide ranging uses of the modern scientific community. A short section describes the hardware of the system including the probe forming system, the X-ray detecting equipment and the correction procedures applied iteratively during the final processing stages.

1.2.1 History and Development

The first decades of the 20th century saw real developments in the field of X-Ray analysis. Moseley first established the relationship between wavelength and atomic number, using a crystal diffraction spectrometer to gain enhanced resolution of spectra (Reed, 1993). Moseley’s law states that the height of the output pulse is proportional to the energy of the X-ray quantum. The energy of the X-ray is inversely related to the wavelength.

With the development of the Scanning Electron Microscope (SEM), more finely focused electron beams were a possibility. Castaing’s research (1951, quoted in Cescas et al., 1968), was primarily concerned with developing microprobe analysis and laid the theoretical and practical foundations of quantitative analysis. A major recent development was the implementation of silicon lithium, Si(Li), drifted detectors (see page 5). The utilisation of Multi-Channel Analyser (MCA) technology allowed energy spectrum analysis over a range of X-ray energies (Cescas et al., 1968).
1.2.2 Uses

There has been a huge increase in the use of EDMA since the 1960s in such widely based disciplines as dentistry (Gerard et al., 1990; Wiesmann et al., 1993); forensic science (Andrasko and Petterson, 1991; Burnett, 1991; Degaetano et al., 1992; Thornton, 1994); materials science and engineering (Fritsch and Keimel, 1991; Buarzaiga and Thorpe, 1994; Chow and Fung, 1994); and the natural sciences: soil studies (Smart, 1973; Scott and Collinson, 1978; Tovey and Wong, 1978; Smart and Tovey, 1981); geology and mineralogy (Kiel and Fredriksson, 1964; Straszheim et al., 1988; Kwiecinska et al., 1992). This project seeks to develop the technique in the analysis and interpretation of Holocene sediment in a range of different locations in south west England.

1.2.3 The physics of the system

Principles

The probe forming system (Fig. 1.1) consists of a sealed column held under a constant high vacuum to prevent beam scattering (> 10^4 Torr). A tungsten filament at the top of the column is heated to 2700K. Electrons are produced by thermionic emission and accelerated away from the filament by the application of a high negative potential between the filament and the anode (accelerating voltage, \( E_0 \)). The beam is shaped electrostatically by a Wehnelt cylinder (cathode), to a diameter ranging from ca. 10-50\( \mu \)m (Lawes, 1987). The overall performance of the microprobe is related to beam diameter, which is controlled by condensers to produce a narrow diameter beam. For a more detailed description of the principles see Hren et al. (1979), Goldstein et al. (1981), Russ (1984) and Reed (1993).

Quantitative analysis requires a normal incident electron beam to be focused on the surface of the sample. However, there are a number of factors which need correction: chromatic aberration due to drifts in the accelerating voltage; spherical aberrations caused by off axis electrons being of stronger energy than those closer to the beam axis; and, astigmatism created by imperfections in the lens polepieces, which may be corrected with relative ease using the stigmator mechanism.

The sample stage is composed of an earthed plate, with a sample holder. The stage is capable of shifts in the X, Y and Z axes, as well as tilt relative to the detector (normally set at 45° - Yakowitz and Heinrich, 1968), and rotation through 360°.
Figure 1.1  The probe forming system of EDMA.  
(Gill, 1986)
Figure 1.2 Interactions occurring upon electron bombardment of a sample. Principle interactions utilised in the analysis of sediment samples by EDMA are shown in italics.

(Modified from Cescas et al., 1968)
Sample interactions

The high energy incident electron beam travels through the probe column, and is focused on the surface of the sample. Upon impact a number of interactions occur (Fig. 1.2) resulting in the production of:

(i) Unscattered electrons - very high energy electrons which pass straight through the specimen with no interaction (of no use to the analysis).

(ii) Elastically scattered electrons - produced when the electrons in the beam pass very close to the nucleus, thus deflecting the beam (with an energy loss of <1 eV). The angle of deflection is dependant upon the energy of the incident electron. Backscattered electron images contain information relating to the average elemental composition of the sample, since scattering is a function of atomic structure.

(iii) Secondary electron emission - the incident beam may knock loosely bound electrons from the sample. If these are released within 10nm of the surface they will escape as low energy secondary electrons. These are useful for topographical mapping of samples (Lawes, 1987).

(iv) Auger electrons - have limited use in SEM imaging; see Russ (1984: p.6).

(v) X-Rays.

The latter is of prime importance in EDMA, and will be discussed in the following sections.

A brief discussion of atomic structure is required at this point. All matter is composed of atoms, these atoms are in turn composed of smaller particles: protons and neutrons, forming the nucleus of the atom, with electrons orbiting the nucleus in an arrangement of shells. In X-ray analysis these shells are designated K, L, M etc. arranged in order of increasing distance from the nucleus. The electrons in the inner shell (K) are most tightly bound and consequently require the most energy to displace them (Fig. 1.3).

The incident electron beam may interact with an atom in the sample, causing one of the shell electrons to be ejected leaving the atom in an ionised state. The atom will seek to attain ground state as quickly as possible by drawing an electron from an outer shell to fill the vacancy. The movement from an outer shell to an inner shell will create a displacement of energy equal to the difference in energy between the shells involved in the transition (Jenkins et al., 1981). This energy is released as a photon of electromagnetic energy: an X-Ray.
There are essentially two forms of X-ray: (i) characteristic; and (ii) continuum or Bremsstrahlung ('braking' radiation). The former is of prime importance since it contains information which relates specifically to the elemental composition of the sample. Each electron shell in the sample has a distinct energy, which varies with the atomic number for each component in the sample. When an electron transition occurs the amount of energy released will be unique for each element; by counting the X-rays produced at each energy level an indication of the elemental composition of the sample may be gained. X-rays are grouped together into families which denote where they originated, and consequently their energy level. K families are the most abundant i.e. those electrons which fill vacancies in the K shell of the atom, they are labelled Kα, KB etc. A Kα electron will have come from the next shell out from the nucleus (the L shell), while KB electrons will have originated in the M shell. Similar families exist for the L and M shells labelled α, β, τ etc. (Fig. 1.3).

The X-ray continuum may be described as the background signal upon which characteristic X-rays are superimposed. It is created when the incident electron beam is slowed as it passes close to the nucleus of an atom in the sample. Some of the electron’s energy is given up and produces X-rays; the formation of which is a function of atomic number. More X-rays are produced by lighter elements, resulting in a greater proportion of total X-rays at the lower end of the energy spectrum.

An important point relevant to the production of X-rays is the concept of critical excitation potentials (Ec). This relates to the energy required to displace a bound electron from its inner shell position, creating ionisation of the atom and X-ray production. Typically, Eb should be 1.5 to 2 times as large as the Ec of the elements under investigation (Wittry, 1958; Goldstein et al., 1981; Reed, 1993).

Detector system

The detector system is composed of a number of different elements (Fig. 1.4). The detector is mounted on a cold-stage which is housed inside a liquid nitrogen dewar (-190°C). This prevents redistribution of the Li within the Si, and helps reduce noise. The detector itself is constructed from Si which is doped with small quantities of Li, and is often described as ‘Si(Li) drifted’. Ultra thin gold contacts are evaporated on to each end of the crystal (Lawes, 1987; Statham, 1980). X-rays emitted from the sample travel in all directions in the vacuum chamber, some will be directed towards the detector. Those with sufficient energy will penetrate the Be window (ca. 8μm), impact upon the Si(Li) surface and cause a charge to be liberated which is directly proportional to the
Figure 1.3 Arrangement of K, L and M shells, with associated X-ray families.
Figure 1.4 Detector system. The detector is held at a constant temperature of 100K using liquid nitrogen. X-rays enter through the Be window and impact upon the Si(Li) crystal surface. Electrical pulses are collected by a field effect transistor, amplified, processed and stored in the analyser’s memory.
incident photon energy. This charge is collected by applying a high voltage (500-1000V) between the contacts. The electron charge from each X-ray is passed to a field effect transistor (FET), which produces a small electrical pulse. This signal is amplified and undergoes a number of processing operations before being passed to the MCA, where it is stored. The MCA records the intensity of each pulse alongside its energy level. After a predetermined time has elapsed, the live-time, an X-ray energy spectrum is produced by plotting the number of X-rays counted at each given energy level (Erasmus, 1978; Statham, 1980; Goldstein et al., 1981; Reed, 1993 - chapter 11), Fig. 1.5.

There are a number of small problems inherent to the use of this type of detector. Any surface which is 'visible' to the detector is a potential source of spurious radiation. The detector has a dead time caused by the fact that the processing time is greater than the conversion time of the MCA, therefore the system is ineffective for a length of time while each pulse is collected and passed through the processing system.

1.2.4 Correction procedures

Castaing recognised a number of complications in the application of electron microprobe technology to analytical procedures (Cescas et al., 1968). In the conversion of X-ray intensity to mass concentration there is a difficulty since intensities measured by the detector are not the true intensities generated within the sample. A number of correction procedures must be applied to gain true intensities.

Initial corrections for dead time, drift and contamination, and background should be carried out prior to analysis. Matrix correction procedures are then applied to adjust for: (i) differences in atomic number (Z) since the generation of X-rays varies with the elemental composition of the sample - this correction procedure deals with the penetration and scattering of electrons as they ionise. The effect if uncorrected would lead to a reduced apparent concentration of heavier elements and increased concentration of light elements; (ii) changes in absorption characteristics with different elements in the sample (A), since absorption of X-rays in a sample is controlled by their depth distribution and the absorption coefficients of each element present in the sample. Only X-rays that leave the sample are useful to the analysis. As the X-rays pass through the sample they will be absorbed exponentially with distance travelled; and (iii) differences with respect to the fluorescence of atomic nuclei within the sample (F). This is due to the fact that absorption of X-rays in a sample by one element will
Figure 1.5  Results gained from analysing a suspected diatom frustule from a depth of 8.10m in the North Sands sedimentary sequence.
result in the excitation of another. Thus, a proportion of the measured intensity from a given element will be increased by this secondary excitation. The extent to which the X-ray intensity is increased is a function of the other elements present in the sample matrix. This effect is greatest when the energy of the fluorescing radiation falls below the absorption edge of a corresponding analytical line. These factors will have different relative impacts on samples of different composition and structure.

The ZAF corrections are applied iteratively until results are statistically acceptable. The user must carry out regular calibration of the microprobe using a stub of known composition, (e.g. Co), to limit problems caused by detector drift and contamination. This procedure ensures optimal analysis conditions are maintained throughout the analyses.

1.2.5 Accuracy

Cescas et al. (1968) state that care must be taken to ensure that the precision of collection is greater than the errors in the correction procedures employed. During analysis care must be taken to use the same operating conditions for all samples analysed (E₀, tilt angle, probe current).

Generally the detection limits, defined as the concentration of element required to produce an intensity three times as large as the standard deviation of the background, will vary for the sample under investigation (matrix structure, composition). Published figures range from 0.1 to 0.01% weight fraction (Erasmus, 1978). Statham (1980) suggests for Z between 11 and 30 (Na to Zn) the detection limit is 0.1%wt with greater than 3x10⁴ counts, although the low end of the energy spectrum will exhibit higher detection limits due to greater absorption of electrons within the sample. When analysing bulk samples with a total analysed volume between 10-50μm³, detection of small elemental amounts will be difficult (Erasmus, 1978).

C.A. Anderson (1967) suggests that the quality of analysis depends upon the degree of spatial resolution, the sensitivity of detection and the precision of measurement (Table 1.1). Goldstein et al. (1981) state that, although the technique of EDMA may be precise and accurate, the characteristics of some materials may limit the accuracy to ±10% relative to the true value, due to variable surface geometry and roughness. There may also be inaccuracies introduced during the analysis by radiation damage to the sample i.e. loss of mass (Hall and Gupta, 1974), production of CO₂, H₂, NO₂, contamination resulting in the deposition of hydrocarbons (Erasmus, 1978).
**Precision:** Measurements that relate to scatter of dispersion among test results without assumption of any prior information

1. Statistics of X-ray counting
   a. Signal from unknown
   b. Signal from reference standard
   c. Background measurements
   d. Calibration measurements

2. Other sources of scatter
   a. Stability of electronics
   b. Sample positioning (reproducibility of 'focus')
   c. Sample preparation (surface roughness or irregularities)

**Accuracy:** Measurements that relate to differences between average test results and true results when the latter is known or assumed

1. Error in relative intensity
   a. Sample preparation
   b. Background measurements
   c. Counting system errors (dead time error, peak shift)

2. Error in calibration
   a. Empirical method: accuracy of equations; uncertainty in true composition
   b. Computational methods: accuracy of equations; uncertainty in physical properties (absorption coefficients; X-ray yields; etc.)

Table 1.1 The different factors which affect accuracy and precision of EDMA results (From Cescas *et al.*, 1968).
1.3 Alternatives to EDMA

There are a number of different geochemical techniques available for the investigation of palaeoenvironmental signals in peatlands. This research sought to investigate EDMA in the analysis and interpretation of these signals. However, a number of problems are associated with the technique and the way in which it produces data, which are the focus for discussion later. The major problem associated with EDMA data is that the system yields elemental data which are expressed as a proportion of all of the elements under investigation. This has been noted by some workers (Grattan, 1994; Pyatt et al., 1995) as a potential limitation, and means direct comparison between the results from EDMA and other more conventional bulk chemical methods is not possible (Erasmus, 1978). However, the technique has illustrated the potential to reveal much information based on general elemental trends. Indeed, Pennington et al. (1972) state the overall trends in conventional concentration data yield the greatest amount of palaeoenvironmental information.

A number of closely related techniques have been developed and fall under the broad heading of X-Ray spectrometric techniques. All share the following stages: (i) excitation of characteristic radiation from the specimen by bombardment with high energy photons, electrons, protons; (ii) detection and integration of the characteristic photons to give a measure of emission line intensity; and (iii) the conversion of the characteristic emission line intensity to elemental concentration by use of a calibration procedure (Jenkins et al., 1981). Three of these are briefly introduced below and compared in Table 1.2.

Wavelength Dispersive Spectrometry (WDS)

As the name suggests, the principle lies in analysing the wavelength of X-rays emitted following bombardment by an electron beam. X-rays produced in the sample are focused on to a diffraction crystal in which the atoms are aligned in a very orderly arrangement. The beam is reflected at a specific angle by the crystal and the X-rays are detected using a gas flow proportional detector. A problem with the method is that each crystal is only operational over a specific wavelength range. Thus, for full element analysis a number of crystals must be used. This means that analysis for a range of elements, as is required for this research, may be time consuming. Descriptions of the technique may be found in Lawes (1987) and Reed (1993 - chapter 11).

X-Ray fluorescence

This technique relies upon the production of characteristic X-rays as an excitation source radiation
### Table 1.2  Comparison of EDMA, XRF and bulk chemical operations

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<th><strong>Bulk chemistry</strong></th>
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<td><strong>Analysis time</strong></td>
<td>Simultaneously processes X-rays of all energies</td>
<td>Need to scan using a range of crystals through different angles to get full range coverage (time-consuming)</td>
<td>Generally time consuming, full analysis may take a week or more</td>
</tr>
<tr>
<td><strong>Analytical performance</strong></td>
<td>Detector can be placed close to the sample, therefore captures most X-rays</td>
<td>Geometrical restrictions due to X-ray diffraction, size of detector means 80 - 95% of the X-rays are lost during diffraction. Good spectral resolution - peak separation</td>
<td>Variable efficiency with which elements liberated into solution from different types of sediment</td>
</tr>
<tr>
<td><strong>Quality control</strong></td>
<td>No moving parts that require alignment, but requires calibration every 4 samples</td>
<td>Need to frequently change crystals, much re-calibration required</td>
<td>Much equipment required, frequent quality control checks necessary</td>
</tr>
<tr>
<td><strong>Range of elements</strong></td>
<td>Detects Z&gt;11 with Be window; Z&gt;5 without</td>
<td>Detects Z&gt;4</td>
<td>Costly, therefore means frequently that only a small range of elements are analysed</td>
</tr>
<tr>
<td><strong>Data format</strong></td>
<td>Produces data as % of analysed volume. EDS XRF = ppm</td>
<td>Produces data as % of analysed volume and in ppm</td>
<td>Presents concentration data in ppm</td>
</tr>
</tbody>
</table>
which is obtained directly from fluorescence of the anode in an X-ray tube. Electrons are emitted from a heated cathode, accelerated and focused to strike the anode. Upon impact most of the power is lost as heat, with only a small amount of energy resulting in the emission of X-rays. It is these X-rays which interact with the atoms of the sample and produce further characteristic X-rays which relate specifically to the elemental composition of the specimen (Jenkins, 1974; Williams, 1987). Common anode materials include chromium, rhodium, tungsten and molybdenum (Jenkins et al., 1981) amongst a number of other suitable elements. This technique developed largely as a wavelength dispersive method (WDS), but energy dispersive (EDS) forms are common with a greater flexibility offered by the superior energy resolution capabilities of the solid state detector, and the simultaneous, as opposed to sequential, collection and processing procedures speeding analysis times considerably (Williams, 1987).

A new development of this technology is the introduction of EMMA (Energy dispersive Multi-element Miniprobe Analyser). This is variation on the energy dispersive XRF technique which utilises monochromatic X-ray radiation as an excitation source, and is thus capable of reliable trace element analysis for a limited range of elements (Cheburkin and Shotyk, 1996).

**Bulk chemical operation**

Previous palaeoenvironmental investigations have used bulk chemical procedures to obtain the required geochemical data (e.g. Mackereth 1965, 1966; Mønsjo, 1968; Pennington et al., 1972; Mannion, 1978, 1979; Livett et al., 1979; Van Geel et al., 1989; Bennett et al., 1992; Shotyk, 1996a; Shotyk et al., 1996). This involves subjecting each sample to a time consuming and frequently hazardous operation, involving chemical digestion and subsequent analysis using a suite of different pieces of analytical equipment including atomic absorption spectrophotometers (AAS), flame photometers, and inductively coupled plasma mass spectrophotometers (ICP-MS). Descriptions of these techniques are outside the context of this thesis, but further details may be obtained elsewhere (Date and Gray, 1989; Jarvis et al., 1992; Ure, 1995).

Bengtsson and Enell (1986) state that chemical operations are frequently dependant upon the material analysed. A common problem is that the results obtained from different methods may be unreliable and not directly comparable. The results should be treated with a degree of caution. Although they produce concentrations of elements (ppm) the overall question of efficiency of the
extractant method used to liberate each element into solution must be addressed, as must the accuracy of the analytical technique. Bengtsson and Enell (1986) propose a standard reference technique for use in palaeoenvironmental work. This technique was adopted for comparative analysis of the North Sands sediment, the results of which will be discussed in Chapters 3 and 4.

1.4 Uses of EDMA in palaeoenvironmental reconstruction

The use of EDMA in palaeoenvironmental reconstruction is in its infancy. The primary application of the technique is to gain geochemical data relating to palaeoenvironmental conditions to aid interpretation of specific processes. However, the greatest information is obtained when the method is used in association with other data, such as pollen and diatoms, with a secure chronology provided by radiocarbon dates.

Pyatt et al. (1991) first used the technique in a palaeoenvironmental context applying it to the analysis of the remains of a 2000 year old bog body from Lindow Moss. The technique was utilised to illustrate the mobility of elements between the body and the encompassing peat mass. It provided a useful indication of the relative mobility of the elements under investigation and served “to illustrate all the important geochemical trends....” (Pyatt et al. 1991: 155). The technique was put to a similar use by Bartsiokas and Day (1993), who used it on fossil bone samples from Java. They adopted a new method for sample preparation and used peak-to-background ratios (Erasmus, 1978; Statham and Pawley, 1978; Small et al., 1979; Statham, 1979) as the basis for analysis, concluding that EDMA is an accurate technique for studying the elemental composition of various materials. However, these workers did not use the technique for direct palaeoenvironmental reconstruction, and it was not until the work of Grattan (1994) and Grattan et al. (1996) that the procedure was first adopted in an investigation of Holocene environmental development. He applied EDMA to both lake and terrestrial sediments in northern Scotland to investigate environmental development and anthropogenic impacts from deforestation and pollution episodes. Grattan found the technique to produce comparable results to those obtained using other bulk geochemical techniques from similar sedimentary environments in the locality (e.g. Bennett et al., 1992). Pyatt et al. (1995) used EDMA in association with diatom analysis to examine soil changes, erosion and acidification episodes as the result of climate change, catchment vegetation succession and anthropogenic disturbance as recorded in sediments obtained from Loch Hellisdale, northern Scotland. Charman et al. (1995) similarly investigated sediments from northern Scotland, using pollen analysis and EDMA to examine the
environmental effect of three separate tephra deposition episodes.

1.5 Interpretation of individual elements for EDMA

Bengtsson and Enell (1986) state that a body of sediment may be regarded as a mirror of past conditions in ecosystems and in the surrounding land. Systematic analysis of the sediment may elucidate environmental processes operating both externally (allogenically), including such factors as climate change, anthropogenic activity, and internally (autogenically), including those processes which govern the development and accumulation of the sediment, microbial activity, mobilisation and precipitation of certain elements and changes in the redox state of the system (Jones and Bowser, 1978). Autogenic compounds may include biochemically precipitated carbonate minerals, amorphous and cryptocrystalline Fe and Mn, oxyhydroxides, sulphides, phosphates etc. (Engstrom and Wright, 1984).

The quality of any inferences drawn from the geochemical data collected will be as accurate as: (i) the reliability of the analytical procedure, and (ii) the way in which the data are interpreted to produce the environmental reconstruction model. The former of these will be addressed elsewhere with respect to EDMA (Chapter 3). A discussion of the latter follows.

There have been many palaeolimnological studies which use geochemistry as the primary data source. The investigations of the British Lake District and Scotland are the most notable (see, for example, Mackereth, 1965, 1966; Pennington et al. 1972; Pennington, 1981; Bennett et al., 1990; Edwards and Rowntree, 1980; Grattan, 1994). Mackereth (1965) largely initiated chemical investigations of lake sediments, suggesting that the composition of the sedimented material is indicative of the stability/instability of the land surface from which it was derived. His analyses of the Lake District sediments led him to a number of conclusions:

“One may then regard the sedimentary sequence of a lake deposit as a series of samples of soils eroded from the drainage basin and deposited chronologically in the lake bed.” (Mackereth, 1966: 168).

There have been many palaeoenvironmental investigations using the geochemical signals held within a body of peat as a primary information source (Livett et. al., 1979; Glooschenko, 1986; Van Geel et al., 1989; Grattan, 1994; Shotyk et al., 1996). There appears to be a great deal of potential in such investigations (Livett, 1988) since the sediment is a store of both allogenic and autogenic
materials, and as such may provide an insight to the processes operational during different accumulation phases of the peat system, and those processes which influence the sediment unit externally. Grattan (1994: 246) states “... EDMA to mire, as opposed to lake sediments, allows the reconstruction of general environmental trends and specific episodes of environmental disturbance”.

The chemistry of a peat body relates to the composition of the original plant material, the supply of solutes and particulates (from both atmospheric and groundwater sources), the extent and nature of biological activity and the environmental conditions (pH, Eh, temperature) during and after peat formation (Clymo, 1983; Naucke et al., 1993). Inferences drawn from geochemical data will have to take account of the relative importance of a large number of dynamic, inter-related factors (Fig. 1.6).

Kemp et al. (1976) suggests the following classification for the majority of elements analysed in palaeoenvironmental studies, although many of these elements may be considered components of more than one group:

<table>
<thead>
<tr>
<th>Major elements:</th>
<th>Na, K, Mg, Si, Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate elements:</td>
<td>Ca, Mg, inorganic C (carbonate)</td>
</tr>
<tr>
<td>Nutrient elements:</td>
<td>organic C, N, P</td>
</tr>
<tr>
<td>Mobile elements:</td>
<td>Fe, Mn, S</td>
</tr>
<tr>
<td>Trace/heavy metal elements:</td>
<td>Cu, Pb, Zn, Sn, V</td>
</tr>
</tbody>
</table>

This classification will form the background to the analysis of elements in this study, with data generally presented in the above groups to aid interpretation and provide consistency.

1.5.1 Major elements

Sodium (Na)

Sodium is a highly soluble, alkali metal. It is present in all outer spheres of the Earth, and has an abundance of approximately 25000 ppm (Day, 1963; Wedepohl, 1995). In the main modes of occurrence sodium may be found in a limited number of complex aluminohalide minerals; in a very large group of complex silicate minerals, typically associated with igneous rocks; and, in a variety of soluble salts. In igneous rocks it may be appear as orthoclase, albite and anorthite (Day, 1963). When associated with mineral matter in peatland sediments it is indicative of the relative importance of leaching and erosion. If there is a high proportion of the element in the mineral fraction it provides
Figure 1.6 Origin of the sedimentary geochemical record
evidence for soil erosion. Conversely, when there is a low proportion of the metal associated with mineral material, it suggests that soil maturation and leaching processes are occurring under more stable environmental conditions (Mackereth, 1965; 1966; Pennington et al., 1972; Guppy and Happey-Wood, 1978; Mannion, 1979; Edwards and Rowntree, 1980; Pennington, 1981; Engstrom and Wright, 1984; Gill, 1989; Bennett et al., 1990; Grattan, 1994). Na has a low affinity for organic substances and forms weak organic complexes, and thus may be rapidly lost from peatland systems (Shotyk, 1988). Damman (1978) studied a number of elements, finding Na to be the element most rapidly and completely removed from the peat. Clymo et al. (1990) comment that generally less than 1% was retained in cores from Scottish rainwater-dependent peatlands. Na maybe associated with salt water influence upon a coastal catchment, especially when it exhibits a relationship to K (Bengtsson and Enell, 1986). The concentration of dissolved Na in soil may be related to the amount of rain, the rate of evaporation, the drainage regime, which is in turn controlled by climate, topography and the texture of the soil (Goldschmidt, 1954). Na normally forms a higher proportion of total ionic content of oligotrophic/ombrotrophic waters, due to its relative abundance in rainwater (Green and Pearson, 1977).

**Potassium (K)**

Potassium has a strong affinity for O and the halogens, and occurs primarily with these elements in nature. There are a large number of K containing minerals, including biotite, feldspar and hornblende, in which K forms a major component, together with a large number in which the element occurs as a more conservative constituent. In igneous rocks the element reaches between 3-4%, with an average crustal abundance of 133 ppm (Wedepohl, 1978). The weathering of K-feldspar, which is a function of pH, and the concentration of Si and Al in solution, releases much K into the soil solution. This is either used in the formation of K minerals, absorbed by clay particles or removed by fluid migration. In the mineral phase it may be used as an indicator of mechanical erosion of basement materials, and often follows the same distributional pattern as Na. It is important in mire ecosystems as a plant nutrient (Naucke et al., 1993), where it is generally in a mobile form and may be readily leached (Athi, 1984). According to Goldschmidt (1954), the geochemistry of K ions in soils is dominated by the equilibrium of cation absorption and exchange between soil solution and various clay minerals. Shotyk (1988) notes strong bio-accumulation of K in surface peats, but below the acrotelm layer of the mire the element may be readily leached since it exhibits a low humic/fulvic acid complexing capability. Aulio (1980) studied 13 separate Sphagnum species for a range of
different elements and discovered the greatest element in concentration was K, confirming the strong bio-accumulation for K of moss species. Generally K forms a greater component than Na in sedimentary sequences (Mackereth, 1966).

Magnesium (Mg)

This alkaline earth element is an abundant element in nature, accounting for 2.2% of the continental crust. There are numerous minerals which contain this element, of which forsterite is the pure orthosilicate form, and olivine the more general form in rock (Day, 1963). It may reflect the process of weathering, soil formation and sedimentation (Goldschmidt, 1954). It is an indispensable element to plant life, being an essential constituent of chlorophyll (Gill, 1989; Goldschmidt, 1954). Mg is a very soluble element and forms divalent cations in aqueous solutions (Sikora and Keeney, 1983). It is similar to Na, K and Ca in that the adsorption of the element by decomposing organic matter is not particularly strong, and forms unstable organic complexes which are readily leached from the peat, especially if the pH of the circulating water is low. However, Damman (1978), studying ombrotrophic peat bogs found this element accumulated to the greatest extent with respect to the peat mass as a whole.

Mg$^{2+}$ is the second most abundant cation in sea-water (Gill, 1989) and may reflect salt-water influence upon a catchment (Bengtsson and Enell, 1986).

Calcium (Ca)

Calcium, occurs in the upper crust at about 3.5% by weight forming a large number of minerals, some of which are major constituents of rocks. In most minerals and other inorganic materials Ca forms bonds with the strongly electronegative elements O and F. It occurs in minerals primarily as silicates, carbonates, phosphates, sulphates and borates, with the most common Ca bearing forms including plagioclase feldspar, pyroxene and amphibole. Its abundance in granitic rocks is around 0.72-1.33% wt CaO. The concentration of dissolved Ca in natural waters is controlled by the level of dissolved carbonate, phosphate and sulphate species (Wedepohl, 1978). The mineral form in sedimentary systems frequently shows a similarity to K, Mg and Na possibly indicating periods of mechanical erosion, however, it is more easily removed in solution than these. Hence, it may only be representative of mechanical erosion during extreme environmental events. The highest concentration of the element in the sediment of the Lake District was immediately after deglaciation
Mannion (1979) states that low levels of Ca may suggest leaching processes are active.

High H ion concentration favours the mobility and therefore the removal of Ca via leaching processes (Goldschmidt, 1954; Shotyk, 1988). This element has a strong affinity with organic ligands (humic and fulvic acids) and as such a body of sediment may contain much Ca not associated with allogenesis (Engstrom and Wright, 1984). Ca\(^{2+}\) is the main cation in the exchange complex, and thus effectively controls pH (McRae, 1988). Zailer and Wilk (1907) used the Ca/Mg ratio to distinguish between ombrotrophic and minerotrophic mires, a low value indicating a bog and a high value indicating fen conditions. Witting (1947) suggests the boundary between bog and fen occurs at around 1 mg l\(^{-1}\) Ca.

**Silicon (Si)**

Silicon is one of the most abundant crustal elements, and is a major constituent of most common rock forming minerals: silicates and aluino-silicates. The most common silicates are quartz, feldspar and mica, these frequently forming a significant component of detrital material. The abundance of silica in igneous rocks of the crust range from 35 to 85%, with granites accounting for 72.1% on average (Wedepohl, 1978, 1995). It most commonly occurs in the oxidised state as SiO\(_2\). The element is often derived in large proportions from erosion of exposed soils (Goldschmidt, 1954; Shotyk, 1988; Pyatt et al., 1992). Quartz in sediments may represent the inclusion of wind-blown dust, for example under peri-glacial conditions (Goldschmidt, 1954; Cowgill and Hutchinson, 1970). Davis et al. (1984) suggest silica and associated minerals may originate in peat by a number of different mechanisms: allogenic detrital contributions in the form of insoluble quartz and other silicates and aluino-silicates; autogenic formation during sedimentation; soluble biogenic silica from plants; post-depositional and diagenetic alteration of existing minerals. Silica may occur as associations with aluino-silicate minerals (Cowgill and Hutchinson, 1970), or in the form of opaline silica skeletons of plants and animals (phytoliths, diatoms frustules, radiolaria, chrysophyte cysts, sponge spicules). The limiting factors for the latter are usually N and P (Goldschmidt, 1954; Engstrom and Wright, 1984; Grattan, 1994).

It is useful in palaeoenvironmental interpretations to separate the allogenic/autogenic fractions of SiO\(_2\) (Feustel and Byers, 1930 - quoted in Shotyk, 1988; Chapman, 1964; Engstrom and Wright,
1984), and commonly values in the region of 8% soluble, 30% insoluble are found in peatland systems (Shotyk, 1988). Davis et al. (1984) state that separation is possible by inference from compositional, textural and geochemical evidence including crystal morphology, the presence of other mineral inclusions and the composition of the mineral itself. Mønsjø (1968) suggests that high levels of SiO2 with Ca and Fe indicate the influence of mineral soil water during the formation of carr peat. He also proposes that increased levels of SiO2 with Fe and Al in the uppermost sediments may relate to the deposition of airborne mineral particles.

Aluminium (Al)

This element is the dominant metal in the earth’s crust. It occurs as cryolite, chiolite, elpasolite and weberite in granitic rocks, but is a component of a wide variety of different compounds, including kaolinite, a major clay mineral, with orthoclase and albite dominant forms in igneous rocks. Typical abundances for the element in the crust approach 80,000 ppm, or 7.96% (Day, 1963; Wedepohl, 1995). A common weathering effect of aluminous minerals following dissolution is that the cations are leached out, with the Al and Si undergoing hydrolysis and subsequent recombination to yield aluminium silicate clay minerals of some form (Day, 1993). It is primarily viewed as an element indicative of erosional intensity and soil leaching, with minimal post depositional diagenesis, since its chemistry is not affected by redox conditions or sulphide concentrations (Engstrom and Wright, 1984; Clymo et al., 1990). According to Bache (1986), the solubility of the cation is dependant on pH, rising rapidly below pH 5. However, Muscutt et al. (1993) illustrated the concentration of organically complexed Al species to show a strong correlation with dissolved organic carbon (DOC), concluding that acidity was not the major control of Al in the streamwater of the Plynlimon catchment. In the presence of organic matter Al will move into solution, where it is leached from the upper surface humic layers and precipitated further down the profile. Bache (1986) states the cation exchange system of acid soils provides a large reserve of ionic Al, which can be brought into solution when soluble salts percolate through soils. Thus Al may be commonly utilised as an indicator of acidification, in association with other elements (Bengtsson and Enell, 1986).

Weathered granite may be almost completely devoid of Na and Ca, with partial leaching of K, Mg, Fe³⁺, while Al remains immobile, resulting in very aluminous sediments (Gill, 1989), for example the china clay deposits of Lee Moor, Devon and similar examples throughout Cornwall.
Both SiO₂ and Al may be complexed with other sedimentary components: SiO₂ as an anionic ligand of hydrated Fe and Mn oxides; with Al chelated with high molecular weight humic materials (Engstrom and Wright, 1984).

**Carbon (C)**

Carbon is essential for every form of life. Its abundance in naturally occurring rocks of the crust is around 2000 ppm (Wedepohl, 1995). It is a most ubiquitous element, and is encountered in a great variety of forms and locations: as a free element it is found in the lithosphere; CO₂ is present in the biosphere, the atmosphere, the hydrosphere and the lithosphere (Day, 1963). The most important ionic forms of C in nature are the carbonate and bicarbonate ions, in which state vast quantities of C are immobilised in the upper part of the lithosphere. Numerous carbonate minerals exist, many of which are associated with metals e.g. Na, Ca, Sr, Ba, Zn, Mg, Cd, Pb, Fe, Mn and Co (Day, 1963). According to Gill (1989), sedimentary rocks have on average 0.2-2% organic matter, the highest amount is found in shales. He states that inorganic C occurs largely as carbonate, mainly biogenic in origin. The solubility of inorganic C is governed by the pH of the circulating water and the presence of H₂CO₃ acid (Gill, 1989). Increased production of CO₂ from decaying organic matter will lead to a higher concentration of H₂CO₃ and thus more carbonate is dissolved.

The net difference between primary production and the total decomposition and leaching determines the C balance of a peatland system (Silvola et al., 1996). Natural soils exhibit a net gain of organic substances of generally acidoid character (e.g. humus), which can form compounds with Fe and other metals (Goldschmidt, 1954). Pennington et al. (1972) comment that in a description of Late-glacial sedimentary profiles it is often more informative to use carbon content than any other variable to distinguish minerogenic material. Mackereth (1965) states that similarities in the element between two very different lakes shows that the controlling factors are regional, confirming the importance of C as a sedimentary variable (Steinberg et al. 1991). Kuhry and Vitt (1996) have used fossil C/N ratios as a measure of peat decomposition over a 9000 year period.

DOC generally includes both simple organic compounds, such as carbohydrates and short chain acids, as well as more complex humic and fulvic complexes (Heyes and Moore, 1992). Peatland investigations have confirmed that the deeper peats are generally more resistant to decay processes, with the bulk of CO₂ production confined to the acrotelm layer only (Hogg et al., 1992). If there is a
net loss of CO₂ to the atmosphere or by transformation to another product, this may influence the pH regime of the system, with a subsequent effect on the availability of certain mineral nutrients in waterlogged soils (Sikora and Keeney, 1983).

1.5.2 Nutrient elements

Phosphorus (P)

The most abundant phosphate mineral in the crust is apatite, which is frequently associated with silicate rocks. The only stable oxidation state of phosphorus within the lithosphere is the P⁵⁺ state of the phosphate ion [PO₄]³⁻. The abundance of P⁰ in common igneous rocks is between 0 and 2%, and in granites between 0.01 to 0.28% (Wedepohl, 1978). The weathering behaviour of the element depends largely upon the kind of P minerals present, and the relative solubilities of these compounds in the weathering solutions. Generally, in acidic environments apatites are remarkably soluble. The concentration of P may thus be regarded as a function of the following variables: (i) the rate of supply; (ii) the efficiency of precipitating mechanisms; (iii) the rate of sediment accumulation; and (iv) the rate of loss of P from recently sedimented material (Mackereth, 1966).

The sedimentation of P may be initiated by a number of factors: (i) carried in solution with Fe and Mn (under anaerobis); and (ii) precipitated into organic material. The first is important both to the precipitation, as well as the retention of the element in the sediment (Mackereth, 1966). Shotyk (1988) states the geochemistry of P in mire waters is most likely related to the concentration of DOC, Fe and the pH, with the capacity of peat to uptake P essentially a function of mineral content (Naucke et al., 1993). Organic P is expected to dominate in peatland systems, therefore the availability of inorganic forms is largely a function of the net mineralisation of organic P and the chemistry of inorganic P in the organic matrix (Sikora and Keeney, 1983). The sedimentary signal of P is often mixed and difficult to interpret since there are many different processes which control the availability of the element. Sedimentation of autogenic P may be through the biological uptake of dissolved inorganic P, with subsequent deposition as particulate organic P (Engstrom and Wright, 1984). In lake, and possibly terrestrial sediments, there may be considerable migration and accumulation of P in surficial layers. The total P content of these layers may bear no relation to the P content of the sedimentary material and may complicate determinations of historical P loading for a particular area (Carignan and Flett, 1981).
I.5.3 Mobile elements

Iron (Fe)

Iron is an abundant element in the lithosphere. It has a high abundance in the earth with a crustal value of 5% (Day, 1963; Wedepohl, 1995). In the crust it occurs in combination with O and freely enters into silicate minerals. Its forms are abundant, widespread and numerous, and include free metallic iron, primary oxide and sulphide minerals and primary silicate minerals, the last of which are extremely numerous, particularly in igneous rocks (Day, 1963). It is an essential element for living organisms. Its presence is strongly affected by the redox potential of the sedimentary environment. Iron is mobilised in anaerobic conditions and precipitated under oxidation (Goldschmidt, 1954; Mackereth, 1966; Jones and Bowser, 1978; Engstrom and Wright, 1984; Naucke et al., 1993). Oxide coatings on sediments (primarily Fe) are ubiquitous in oxygenated environments.

Jones and Bowser (1978) suggest that Fe can be transported in many ways: (i) in a dissolved form as humic/fulvic acid complexes; (ii) in particulate form as inorganic oxides, and oxide coatings on mineral matter from the mechanical erosion of the surrounding soils; or (iii) sedimented by particulate organic matter formed autogenically within the sediment. Soil humic materials play an important role in the mobilisation of Fe since they readily form strong soluble complexes (Jones and Bowser, 1978; Engstrom and Wright, 1984). Mackereth (1965, 1966) and Pennington et al. (1972) have used the Fe:Mn ratio to reconstruct palaeo-redox conditions, a low value being indicative of reducing conditions and a high ratio suggesting the erosion of mineral soils under oxidising conditions. Since the precipitation of the Fe is essentially controlled by the ionic composition of the circulating water, the redox conditions, pH and microbial activity, there may be changes in the long term concentration of the element as the influence of these variables vary with time. A number of workers (Chapman, 1964; Green and Pearson, 1977; Mannion, 1979) suggest that high levels of Fe are indicative of groundwater influence.

Manganese (Mn)

The crustal abundance of this element is eighth in the order of abundance as far as the metals are concerned and is estimated to be 716 ppm (Wedepohl, 1995). It has a number of oxidation states, but is essentially cationic, with states of 2, 3 and 4. It is present in a wide variety of minerals, particularly silicates, where it occurs as a trace or minor element (Day, 1963). It has a geochemistry
similar to that of Fe, with low solubility conditions in aerobic environments and enhanced mobilisation under anaerobic conditions. Anderson and Hawkes (1958) state that ferromagnesian minerals and feldspars decompose fairly rapidly yielding clay minerals and secondary oxides. Goldschmidt (1954) states that Eh and pH are important variables governing the solubility and precipitation of both Mn and Fe. Acidic, anaerobic conditions result in mobilisation, while alkaline, aerobic conditions lead to precipitation. The weathering of crustal rocks is one of the most significant sources of Mn (Jeffries and Snyder, 1981; Engstrom and Wright, 1984). It is an indispensable trace element for organic life and is also an important catalyst in the oxidation of organic matter. Pakarinen and Tolonen (1976) report that the retention of Mn by mosses is rather weak.

**Sulphur (S)**

Sulphur is a primary constituent of three major mineral groups: sulphides, sulphosalts and sulphates, between them forming many minerals. The S content of rock forming silicates is generally less than 100 ppm, however it has been noted as having an abundance of c.330 ppm in granitic rocks (Wedepohl, 1978). Its presence in oxygenated environments is largely controlled by biological processes. The behaviour of the element in the weathering process relates to three main processes: (i) the participation in Eh processes, many of which may influence or be influenced by pH; (ii) the formation of volatile compounds with some light elements, especially H and O; and (iii) its role in a great variety of biochemical processes. In the pore waters of reducing sediments various authigenic metal sulphides will form, the most common of which is FeS (pyrite).

Total sulphur is made up of organically bound S and a wide range of plant available and unavailable inorganic forms (Brown, 1982). Reduced S is an essential element for living creatures (Goldschmidt, 1954; Brown, 1985; Gill, 1989). The source of S may be a combination of the following: (i) mechanical weathering of catchment soils - the S is produced through the microbial reduction of sulphate in terrestrial soils; (ii) the bedrock, this is largely dependant on catchment geology, and; (iii) in more recent sediments from the smelting activities of the 19th century (Pyatt, 1974). Rudd et al. (1986) conclude that the most significant product of sulphate reduction is organic S. Brown (1985) states that 90% of the S (total) in valley mire peats is associated with organic matter, and this was confirmed by the analyses of Casagrande et al. (1980) and Novák and Wieder (1992) in different peat forming environments. Thus sulphate reduction is the major source of S to peatland sediments.
Organic S in peatland systems is commonly found in a C bonded form, including proteins, amino-acids and polypeptides, these are bound to humic acids and colloidal mineral material (Brown, 1982). Inorganic S is less abundant than organic S in sediments, the major form being sulphate in well drained soils. As already introduced, under anaerobic conditions H2S may be produced by bacterial sulphate reduction or by decomposing organic matter. Conversely, when O enters a previously anaerobic environment the sulphides may be chemically and microbiologically oxidised to elemental S, which is then subject to attack by micro-organisms, with the eventual conversion to sulphate (Brown, 1982). However, Casagrande et al. (1977) state that the water content of the soil has much to do with the specific forms of S present.

High levels of S may be detected in more recent sediments as a result of the increased liberation of SO2 into the atmosphere as a result of fossil fuel burning (Cowgill and Hutchinson, 1970; Gill, 1989), this may increase the acidity of the soil system (Goldschmidt, 1954). A greater concentration of S may also be encountered in sediments close to the sea.

1.5.4 Trace/heavy metal elements

These elements are generally the least abundant elements in the rocks of the earth’s crust, and occur in concentrations of less than 1%, frequently below 0.01% or 100 ppm (Alloway, 1995; Wedepohl, 1995).

These elements may be considered as having three roles in the atmosphere, lithosphere and hydrosphere: (i) as nutrients, (ii) as toxic pollutants, and (iii) as indicators of transfer mechanisms (Pierson et al., 1973). It is therefore necessary to determine the background concentrations of these elements to examine the contribution each makes in a particular ecosystem (Fortescue, 1992; Rasmussen, 1996). There is a large amount of literature which proposes that increased levels of a number of trace elements may be attributable to anthropogenic activities (Goodman and Roberts, 1971; Aston et al., 1973; Lee and Tallis, 1973; Pierson et al., 1973; Livett et al., 1979; Van Geel et al., 1989; Christensen and Chien, 1981; Rippey et al., 1982; Glooschenko and Benedetti, 1983; Glooschenko, 1986; Markert and Thorton, 1990; Stewart and Fergusson, 1994; Hong et al., 1994 Renberg et al., 1994; Hong et al., 1996; Shotyk, 1996b). The use of peat profiles for historical monitoring of pollution episodes is a complex process, with some elements proving to be more useful than others (Livett, 1988; Glooschenko, 1986; Stewart and Fergusson, 1994).
Livett et al. (1979) analysed a number of blanket peat profiles for their concentrations of Pb, Zn and Cu, with the underlying assumption that a number of heavy metals will remain virtually immobile once incorporated into the peat. They suggested that a time sequence of deposition may be preserved in the peat profile and dated by pollen analysis. This assumption has subsequently been questioned and there are a number of more complex processes operating which determine the mobility and retention of heavy metal elements in peat (Livett, 1988).

Bog vegetation has long been considered an effective trap of metals both from dry and wet depositional vectors. In particular, species of *Sphagnum* moss have been used to analyse recent aerial pollution and its effects on bog vegetation (Goodman and Roberts, 1971; Glooschenko and Benedetti, 1983; Rühling and Tyler, 1984). The ability of *Sphagnum* species to trap metals is related to a number of factors including the biomass density of its stem, growth rate, leaf structure and its high cation exchange capacity. The last of these factors is attributable to the presence of polyuronic acids in the cell walls (Glooschenko, 1986). Livett (1988) comments that heavy metal-peat associations are initially determined by the surface upon which the metals are deposited. The principal site of accumulation in plants is the cell wall and intracellular membranes. Since many peatlands generally have an abundance of *Sphagnum* species which are incorporated into the developing peat matrix as time progresses, it is likely that any extraneous input of heavy metals will be incorporated into the peat bound to the surficial organic material. Rühling and Tyler (1970) examined the woodland moss *Hylocomium splendens* and found that its capacity for sorption and retention of heavy metals was in the order Cu>Pb>Ni>Co>Mn, Zn.

There are a number of inter-related processes operational in peat which will determine whether a given element will remain bound to the organic matter upon which it was initially deposited, or mobilised to a different location in the profile: (i) the state of decomposition; (ii) the presence of other elements; (iii) Eh; (iv) temperature; (v) the nature of the hydrological regime, especially the position of the water table; (vi) the activity of micro-organism populations; and (vii) pH. Livett (1988) states the last is the most important independent factor to influence heavy metal binding by humic material.

The degree of decomposition has three major effects in peatland environments: (i) loss of organic matter through leaching; (ii) loss of physical structure; and (iii) a change in the chemical state of the
peat (Clymo, 1983). As the peat becomes more humified, the concentration of humic substances increases. These are the major reactive constituents of the sediment and are significant metal binding agents. The association between heavy metal and humic acids is dominated by the cation exchange and chelation process (Livett, 1988).

The pH of the circulating water and peat soil is a particularly important variable in peatlands. The pH will affect the availability of exchange sites, the rates of decay through microbial activity, the availability of plant nutrients and the mobility of Fe, Mn and Al which themselves are important in complexing and chelating processes. Eh will similarly affect the mobility of certain trace elements and is primarily governed by fluctuations in the position of the water table, pH of the circulating water, temperature, the presence of sulphides and O concentration (Clymo, 1983).

The nature of the hydrological regime is of prime consequence in these environments. A peat body fed by groundwater circulation will differ significantly from an ombrotrophic system fed solely by atmospheric inputs. The former mire system will typically be enriched by lithospheric elements gained directly from the surrounding catchment. It will have a higher pH, perhaps approaching neutrality, a more diverse surface flora, greater mobility of nutrient elements, especially in the acrotelm, higher concentrations of major ions since more exchange sites are available for the bases from the groundwater, and generally a more rapid rate of accumulation. The ombrotrophic system will exhibit a much lower pH due to the low availability of Ca and Mg ions (Sikora and Keeney, 1983). The system will experience a lower rate of decay since microbial activity will be restricted, a greater concentration of complexing organic substances produced as a by-product of decomposition, with a smaller contribution from the surface vegetation which may release polyphenolic acids, and a larger concentration of metallic compounds. Durand et al. (1994) illustrated that metal leaching will be higher for acidified systems. Glooschenko (1986) showed metals to be mobile in peat profiles with the water table location and fluctuation being a major influence on metal behaviour.

The presence of other elements is of significant importance. For example, a net decrease of CO2 may exert a major influence upon pH and availability of certain mineral nutrients in the soil (Sikora and Keeney, 1983). They also suggest that Fe and Mn may affect the Eh and pH status of the circulating waters, changing the solubility of certain elements. The formation of sulphides produced primarily from the reduction of sulphates under anaerobic conditions (Brown, 1985; Rudd et al., 1986), may
be responsible for the decreased mobility of certain heavy metal elements such as Zn, Cd, Cu (Hermann and Neumann-Mahlkau, 1985).

It is evident that the accumulating peat matrix is an extremely complex system. Stewart and Fergusson (1994) conclude that the physicochemical processes in peat bogs are not well enough understood to make a definite statement of the origin of certain trace elements, although Markert and Thornton (1990), in their analysis of a number of elements from an English peat bog soil suggested that the vertical transport of heavy metals through such processes as leaching to groundwater was negligible due to the high affinity of the elements for organic matter. They encountered no migration of substances between basal and higher layers. A brief discussion of the geochemistry of the heavy metal elements analysed in this research will now be presented.

**Copper (Cu)**

Copper is a chalcophile element (it has a strong affinity for S). The average crustal for this element is around 25 ppm (Day, 1963; Wedepohl, 1995), with a much lower occurrence in acidic, granitic rocks. It does not contribute significantly to rock-forming silicate minerals, and occurs in rocks largely in the form of sulphides. The presence of sulphate ions and organic matter may lead to the microbial formation of H₂S, and thus to the precipitation of metal sulphides (Goldschmidt, 1954). It is a necessary element for plant and animal life (Baker and Senft, 1995).

The mobility of Cu in peat profiles has been considered in some detail by Tanskanen (1976), who concludes that Cu generally decreases in concentration as the peat becomes more humified, and increases with pH and depth. Merrington and Alloway (1994) conclude that aerial deposition of the metal is the dominant mode of transport from two metalliferous mine sites in the UK. The anthropogenic flux of Cu is said to be important with respect to natural levels, thus the composition of peats associated with the impact of human activity may contain elevated levels of Cu superimposed on background concentrations (Rippey et al., 1982). Cu is said to have an AIF of 1363%. It is one of the elements generally considered to be immobile under anaerobic conditions due

---

1 AIF - Atmospheric Interference Factor (see Lantzy and Mackenzie, 1979)

\[
\text{AIF} = \frac{\text{total anthropogenic emissions}}{\text{total natural emissions}} \times 100
\]

A value of 100% means natural = anthropogenic sources e.g. AIF of 1300% indicates anthropogenic sources are 13 times as large as the natural flux.
most likely to a combination of sulphate reduction and the formation of metal/organic complexes (Livett et al., 1979; Swanson and Johnson, 1980; Hermann and Neumann-Mahlkau, 1985; Shotyk, 1988; Stewart and Fergusson, 1994). Copper has been identified as an indicator of industrial activity (combustion of fossil fuels) increasing in sediments dated from the 19th century (Goodman and Roberts, 1971; Tyler, 1972; Rippey et al., 1982).

**Lead (Pb)**

Lead is a relatively common element in the earth's crust with a general abundance of around 15 ppm (Henderson, 1982; Wedepohl, 1995). It is particularly associated with sulphide bodies, and occurs most commonly in the form of galena (PbS). It is neither an essential nor a beneficial element for plants and animals. It is suggested that soil is a sink for anthropogenic Pb with several well identified sources, including mining and smelting activities, manures and contamination from vehicle exhausts (Davies, 1995; Shotyk et al., 1996). There is little evidence to suggest that Pb is readily lost from soil profiles by leaching processes, indeed it seems that most heavy metals, including Pb, remain in an insoluble, stable form, with the organic soil fraction largely responsible for the immobilisation of the metal (Davies, 1995). Tanskanen (1976) analysed 103 peat profiles from central Lapland and suggested the concentration of this metal increases as pH decreases. In addition Pb is more abundant in less humified peat and exhibits a noticeable surface enrichment possibly due to recent aerial pollution.

However, Pb is considered by some workers to be more mobile in peat profiles than Cu. It may be retained in well drained peat but mobilised and removed in the permanently anaerobic zone below the water table (Damman, 1978), especially where acidity is high and C.E.C. is low (Pakarinen and Tolonen, 1976). Stewart and Fergusson (1994) propose a different hypothesis: in a reducing environment of high organic content with low pH and low Eh, it is likely that Pb(II) would be immobilised by insoluble compounds (e.g. PbS). However, following analysis they found Pb to be mobilised in anaerobic peat, thus suggesting that either there was insufficient sulphide to form PbS, or other elements were more important. Their analyses suggest that Pb displays a relationship with Mn, and consequently may be associated with Fe(III)-Mn(IV) compounds and thus liberated in anaerobic peat. McKenzie (1980) similarly found a relationship between the adsorption of Pb and the oxides of Fe and Mn. He suggests that adsorption by Mn was 40 times greater than by Fe oxides. Glooschenko (1986) and Clymo (1983) noticed a peak at mean water-table level, which effectively
demonstrated the differential mobility of the element under different Eh states.

Pb may be associated with modern aerial pollution from urban/industrial areas such as fossil fuel combustion and pollution from vehicle exhaust, and both modern and prehistoric smelting activities (Tyler, 1972; Pierson et al., 1973; Davies and White, 1981; Rippey et al., 1982; Pacyna, 1987; Nriagu and Pacyna, 1988; Puchelt et al., 1993; Hong et al., 1994; Renberg et al., 1994; Maskall et al., 1995). It has an AIF value of 34,583% (Lantzy and Mackenzie, 1979).

Pollution studies which utilise bog vegetation as indicators of atmospheric pollution (Goodman and Roberts, 1971; Glooschenko, 1986) have noted a regional pattern in the deposition of this metal. Livett et al. (1979) noticed a roughly proportional relationship between log_e population and the surface concentrations of Pb, Cu and Zn. However, the form of Pb compounds released will affect dispersal and inclusion processes. During the earlier smelting operations, the lead released to the atmosphere would have been of a much coarser particulate form, which would have had a lower atmospheric residence time than the aerosol Pb from more recent industrial/urban activities (Grousset et al., 1994). Similarly, much contamination may be caused by wind-blown material from mine waste heaps, especially where the waste is composed of fine material (Davies and White, 1981; Nriagu and Pacyna, 1988; Davies and Ballinger, 1990; Merrington and Alloway, 1994).

Tin (Sn)
There are 10 stable isotopes of this element, greater than for any other element in nature. It is a relatively rare metal with an average crustal abundance of 3 ppm (Day, 1963; Henderson, 1982). The most important natural compound in which it occurs is cassiterite (SnO_2), which is found largely in pneumatolytic and hydrothermal veins associated with siliceous igneous rocks, usually granite (Edwards et al., 1995). Goldschmidt (1954) notes cassiterite to be particularly resistant to weathering and mechanical attrition. However, Sn also occurs in many sulphide ores, stannite (CuFeSnS_3) being the most noteworthy. The occurrence of Sn in peatland systems will be largely from local bedrock sources (Beeson et al., 1977), whether naturally or anthropogenically derived. This metal is among one of the first used in antiquity, with the Cu-Sn alloy, bronze, discovered around 2500 BC (Edwards et al., 1995).

"A great number of tin deposits were known even in ancient times in the south-western and central parts of Europe, such as in Cornwall, ......., all connected with granites of Carboniferous age", Goldschmidt (1954: 392).
In southwest England tin is located in and around the granitic aureole of the Cornubian intruded zones. It has a background concentration of 3-4 ppm in the pelitic rocks of these areas (Beer and Ball, 1986), which compares well with the data of Wedepohl (1995), and those workers mentioned above. Sn is known to have a high affinity for organic fractions, and to be concentrated in humus-rich and organic-rich sediments (Edwards et al., 1995). It is reported to have an AIF of 821%.

**Arsenic (As)**

This element is found predominantly in sulphide ore bodies, of which the most common arsenical mineral is arsenopyrite (FeAsS), but over 200 As-containing minerals have been identified (O'Neill, 1995). In soils the natural levels are dependent upon the nature of the bedrock, with an average concentration of between 1-15 ppm in igneous rocks (Day, 1963; O'Neill, 1995; Wedepohl, 1995). Arsenic may be produced following the combustion of fossil fuels (in particular coal), and as a by-product of the smelting of tin (Harris, 1992) and copper (Lux, 1993; O'Neill, 1995). The majority of As-rich compounds are concentrated in flue dust and soot (Li and Thornton, 1993), with a much smaller component volatilised and transported in the gaseous phase. There is little information relating to its mobility in organic soils, but Christensen and Chien (1981) suggest that As may be incorporated into ferromanganese nodules. Hermann and Neumann-Mahlkau (1985) indicate a mobility comparable with Fe. There is limited evidence to propose As is enriched in humic substances (Hirner et al., 1990). Arsenic has an AIF of 2786% (Lantzy and Mackenzie, 1979).

1.5.5 **Summary**

Peatlands are inherently complex systems with a great number of inter-linked mechanisms operating both as the sediment accumulates and diagenetically afterwards. Hydrology plays a major role in controlling the development of the peat, and consequently may be considered the primary factor governing autogenic processes. There are a number of external influences which may have a significant impact on the peatland ecosystem, each of which operate at different scales. At the macro-scale climate change is the most obvious, but anthropogenic activity also falls into this category. The micro-scale factors include erosion through land disturbance caused by agriculture, deforestation and peat cutting, eutrophication and associated processes.

The systems under investigation are dynamic as the acrotelm is constantly moving upwards as the peat develops. A number of elements may already have been removed before the peat becomes
permanently anoxic (Livett, 1988), thus any description of the chemical changes in a peat profile, must take account of this fact (Glooschenko, 1986).

The above discussion of elements addresses two major issues: (i) to evaluate the usefulness of each to contribute to the overall palaeoenvironmental reconstruction, and (ii) to provide evidence of the relative mobility of different elements at different stages of sediment accumulation, and from different sedimentary environments. Table 1.3 summarises the use of each element in palaeoenvironmental reconstructions.

1.6 Interpretation of multi-element spectra
One of the key advantages of EDMA as an analytical technique is the capability to provide rapid simultaneous multi-element analysis, with no sample destruction. The large amount of data produced necessitates careful investigation of results, since most elements have a variety of different sources. A single element interpreted on its own will not yield a great deal of information and only when a relationship is shown between a number of elements will the interpretation be meaningful. For example, Mg may relate to mechanical weathering of catchment materials, the breakdown of chlorophyll, or give an indication of rainfall intensity (Grattan, 1994). By examining the elements that increase or decrease with Mg an indication of the most likely source may be given. When associated with K it may indicate mechanical erosion, when associated with Na and Cl it may relate to increased rainfall and if it is comparable to P or S it could indicate a source related to the breakdown of chlorophyll.

If the relationship between several elements is maintained over a length of the core their controlling variables may be stable. Differentiation between different sections of the core may also be possible where ratios are maintained, identifying chemizones of distinct composition. Each chemizone can then be regarded as a litho-facies which represents a specific sedimentary environment (Mannion, 1979; Grattan, 1994).

1.6.1 Behavioural trends
Butzer (1982) considered equilibrium concepts of environmental processes which may be utilised in the analysis of EDMA geochemical data. He used a number of terms which require definitions at this stage. Feedback is a change introduced by one variable which is transmitted through the system back
<table>
<thead>
<tr>
<th>Geochemical Group</th>
<th>Element</th>
<th>Main Indicator Value</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Na</td>
<td>Weathering</td>
<td>Absence – leaching</td>
<td>With K = marine influence</td>
</tr>
<tr>
<td>K</td>
<td>Weathering</td>
<td>Bio-accumulation in upper levels, absence – leaching</td>
<td>Marine influence, clay minerals</td>
</tr>
<tr>
<td>Mg</td>
<td>Weathering</td>
<td>Absence – leaching</td>
<td>With Na, K = marine influence</td>
</tr>
<tr>
<td>Biogenic activity - breakdown of chlorophyll</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>Weathering, presence of CaCO₃</td>
<td>Absence – leaching, humic / fulvic acids</td>
<td>Control pH, C.E.C.</td>
</tr>
<tr>
<td>Si</td>
<td>Weathering of exposed soils</td>
<td>Biogenic activity</td>
<td></td>
</tr>
<tr>
<td>Biogenic activity - phytoliths / diatoms / sponge spicules</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Weathering</td>
<td>Acidification, mobilised below pH 5</td>
<td></td>
</tr>
<tr>
<td>Nutrient C</td>
<td>Inorganic – CaCO₃</td>
<td>Organic = humus accumulation</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Inorganic clastic minerals</td>
<td>Biogenic activity</td>
<td>With Fe, Mn = anaerobic conditions</td>
</tr>
<tr>
<td>P</td>
<td>Inorganic clastic minerals</td>
<td>Biogenic activity</td>
<td>With Fe, Mn = anaerobic conditions</td>
</tr>
<tr>
<td>Mobile Fe</td>
<td>Lithospheric materials</td>
<td>Aerobic conditions</td>
<td>Acidity, groundwater influence</td>
</tr>
<tr>
<td>Mn</td>
<td>Lithospheric materials</td>
<td>Aerobic conditions</td>
<td>Acidity</td>
</tr>
<tr>
<td>S</td>
<td>Lithospheric materials, dependent upon geology</td>
<td>Formation of sulphides (anaerobis)</td>
<td>Smelting activities</td>
</tr>
<tr>
<td>Traces Cu</td>
<td>Anthropogenic disturbance (pollution)</td>
<td>Formation of sulphides</td>
<td>Anaerobic catotelm conditions</td>
</tr>
<tr>
<td>Pb</td>
<td>Anthropogenic disturbance (pollution)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Anthropogenic disturbance, SnO₂ exploitation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>Anthropogenic disturbance, SnO₂ exploitation</td>
<td>Anaerobic precipitation if associated with Fe / Mn compounds</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.3 Summary of interpretational possibilities using geochemical data
to the original variable. Negative feedback acts to dampen the effect of the changed variable to maintain stable/dynamic equilibrium, while positive feedback reinforces the effect of externally induced change. Natural systems typically have negative feedback characteristics, exhibiting systems which oscillate around a steady state. This is maintained through a self-regulatory mechanism known as dynamic homeostasis. However, this may be complicated by two factors: (i) secondary responses, in which change continues after the mediating factor has been reversed, for example, water will continue to flow from a hose pipe even after the tap has been switched off, and (ii) thresholds, above which a system is forced to a new dynamic equilibrium. Butzer (1982) discusses a number of different equilibrium states which may be of use in the interpretation of change from EDMA data which will be briefly discussed below (Fig. 1.7):

(i) Static equilibrium represents a stable system which is constant through time. There is no external force which disturbs equilibrium.

(ii) Stable equilibrium is the state in which an initial perturbation from the norm recovers to static conditions after a relaxation period, the variation around the mean may be an integral part of the system.

(iii) Unstable equilibrium involves a change from an old to a new stable state with an accompanying relaxation time. The new level is achieved in the absence of any threshold.

(iv) Metastable conditions with a threshold separating different equilibrium levels may represent external forcing. The threshold could be changing climatic or hydrological conditions.

(v) Steady state conditions represent oscillations around a mean value with no net change in stable conditions. It is not possible to assume significant environmental change.

(vi) Dynamic equilibrium is essentially steady state conditions which exhibit a long-term trend, each deviation from the mean may not be significant but the long term trend is.

Dynamic metastable equilibrium conditions are characterised by long-term trends separated by a threshold to a new dynamic equilibrium level. The establishment of a new level may relate to a significant environmental change.

By considering a group of elements shown to exhibit a degree of correspondence, the above may help in the overall interpretation of palaeoenvironmental change as reflected in the geochemical record.

1.7 Philosophical basis for interpretation

Palaeoecology seeks to initially find the results and then try to reconstruct the courses and conditions
Figure 1.7  Behavioural trends in geochemical data (from Butzer, 1982)
of change which led to them (Rymer, 1978). Its ideological framework is firmly rooted in the Baconian inductive route to scientific enquiry: collection of facts, their ordering, inductive generalisations and preferably theory formulation (Edwards, 1983a; Haines-Young and Petch, 1986). Interpretation of most palaeoecological data is fraught with difficulties, since it is impossible to replicate the conditions of formation to rigidly test if the theories produced are correct.

Popper (1972) states the value of any statement depends ultimately upon its falsifiability. Science is conjecture and refutation. Thus knowledge grows through the elimination of error. The interpretation of palaeoecological data should therefore be consistent with all available facts (statements) and as direct and simple as possible. The principle of uniformitarianism follows logically, in which a continuing uniformity of existing processes is regarded as providing the key to understanding the history of the earth (Gregory, 1989), or to quote Hutton's aphorism: "the present is the key to the past".

Rymer (1978) suggests that methodological uniformitarianism serves as a means of organising our knowledge of the past by serving as an a priori method, limiting interpretations that can be used to explain a given set of data, as such it assumes that the world is regular, lawful and intelligible. A key aspect of the principle lies in the fact that analogy is the main interpretative tool and relies heavily on processes of pattern recognition, with the myriad of statistical techniques which have been developed to aid this process, such as cluster analysis techniques to produce pollen zones that reflect modern communities. A basic question of analogy is how similar must two sets of data be in order to be similar? There is another problem in that every context is unique, no analogy is exact, therefore no argument from analogy is certain (Bell and Walker, 1992). Many former plant communities have different distributions, both geographically and ecologically, to their extant analogues.

There are often a number of possible explanations which can not be distinguished by using the available evidence. Chamberlain (1965) proposed the construction of multiple working hypotheses in these situations, in which weaker theories may be rejected as they are tested critically against each other. Bell and Walker (1992) state the main aim of using multiple hypotheses is to achieve an explanation that is more 'nearly' correct than would have been the case if only a single hypothesis were considered. An example may be cited using an increase in total Si content of a sediment body. This may be associated with (i) an inwash of mineral soil material from the surrounding catchment;
(ii) an increase in biogenic Si, either phytoliths from the catchment vegetation or from in situ diatoms. Only upon further investigation does the explanation become more accurate. Birks and Birks (1980) regard multiple working hypotheses as one of the fundamental philosophical principles of palaeoecology.

Palaeoecologists do not, in general, set out to predict, but to explain. However, the experiments carried out by palaeoecologists do not themselves provide explanation (Rymer, 1978). It is the interpretations that are the key issues and by applying uniformitarianist principles as a conceptual framework the explanations will become more intelligible.

This project will use multiple working hypotheses as a major interpretative tool, since no single statement will ever adequately represent the spectrum of possibilities produced using proxy reconstruction methods.

1.8 Summary

This chapter has introduced EDMA as a palaeoenvironmental tool. Discussion was presented of the development and use of technique in a wide range of applications, illustrating its potential in palaeoenvironmental studies. A large section detailing the interpretation possibilities from geochemical studies was presented, along with the philosophical basis of palaeoenvironmental work of this kind. This leads to the next chapter in which the methodological aspects of the project will be addressed, including a discussion of sites and reasons for their selection.
Chapter 2
Methodology

2.0 Introduction

This chapter presents the methodological aspects of the research. The fieldsites are presented following an introduction to the palaeoenvironmental conditions and archaeology of south west England. Data collection and analysis strategies are introduced, including field and laboratory sampling regimes, and radiocarbon dating procedures.

2.1 South west England and Dartmoor

2.1.1 Geological History

Few geological time periods are unrepresented in the south west peninsula (Fig. 2.1). This is the major reason for its diverse topography ranging from the rugged, dissected rocks of the granitic uplands, to the ‘soft’ landscapes of the Permian, Mesozoic and Cenozoic eras and the wide, gently sloping coastal peneplains formed during Pliocene times (Durrance and Laming, 1982). The oldest rocks of the south west are small exotic masses of Ordovician quartzite and Silurian limestone lying in Devonian beds at Meneage and Nare Head (Edmonds et al., 1975). The largest portion of the land surface is composed of Devonian and Carboniferous rocks, which in places are up to 9km thick (Anderson and Owen, 1980).

The uplands of Dartmoor and Bodmin Moor are the most extensive exposures of the granitic batholith intruded into the sedimentary country rock of Devon and Cornwall during the Carboniferous period following a major period of faulting, folding, metamorphism and granitic intrusion ca. 280 million years ago. The entire area associated with this movement has a tendency for metallic mineral occurrence due to the numerous episodes of faulting and intrusion with subsequent mineral crystallisation. Metallic minerals are distributed in a series of concentric belts around the main aureole centres. The minerals are related both laterally and vertically to the hydrothermal gradients which existed at the time of intrusion between the magma and the much cooler surface rocks. Minerals associated with high temperature crystallisation such as cassiterite, wolfram and tourmaline occur closest to the granite, with more cooler, distant zones forming suitable environments for crystallisation of copper, lead, zinc and iron mineralisations (Edmonds et al., 1975).
Figure 2.1  
Simplified geological map of south west England. 
Modified from Edmonds et al. (1975)
The Quaternary has had a marked effect upon the present day appearance of the environment in the south west. There is currently much discussion as to the maximum extent of glaciation during the Quaternary, with much interest directed upon the sediments around Fremington, north Devon (Croot et al., 1996) and till-like material near St. Martins in the Isles of Scilly (Scourse, 1986, 1991). However, general consensus appears to suggest that the limit of glaciation fell along the north Devon coast during the penultimate cold stage, the Wolstonian (Jones and Keen, 1993; Lowe and Walker, 1997), and that the uplands of the south west were subject, during these cold, glacial episodes to intense periglacial activity (Todd, 1987).

There is widespread evidence for periglacial action in the south west at the coasts and further inland. Abundant solifluction 'head' deposits may be traced throughout the region, characterised by angular comminuted material embedded in a fine matrix. This sedimentary unit is frequently observed at the coasts where it commonly overlies much earlier erosion platforms (Mottershead, 1971; Harris, 1987). Other features of this periglacial era include the upland granite tors with their soliflucted scree slopes ('clitter'). It is suggested that the tors were exposed during periglacial activity of Wolstonian age (Stephens, 1980), with the majority of clutter fields formed during the Devensian, primarily as a result of intense freeze-thaw activity (Kidson, 1971), resulting in partial destruction of the exposed tors. It was during these periods that the extensive alluvial tin deposits were formed in the upland river valleys. The cassiterite (SnO\textsubscript{2}) bearing granite was comminuted under periglacial freeze-thaw action, transported downslope by solifluction processes and deposited in the valleys of many upland river systems. Chemical weathering of the granite releases three main minerals. Biotite, is readily oxidised, feldspars, which are broken down forming clay minerals. Quartz, along with some clay minerals, remains in situ forming a gravel-like deposit known locally as growan (Brunsden and Gerrard, 1977). This material is most likely to have been derived from one of the cold phases of the Pleistocene (Brunsden, 1964), and is encountered in many valleys of this area.

2.1.2 Palaeoenvironments of south west England

A large number of investigations have been conducted into the vegetation and soil history of south west England. These studies have concentrated largely upon the nature, scale and direction of change in the upland zone due to the concentration of suitable sedimentary sites for palaeoenvironmental research. There is obviously a bias in our understanding of environmental change for the south west due to the lack of suitable lowland sites (Caseldine, 1983), although analysis of sediments associated
with archaeological features help piece together the history of these areas (e.g. Carn Euny (Christie, 1978), Colliford Reservoir (Griffith et al., 1984) and Zennor, west Penwith (Herring et al., 1993)).

There are fundamental problems concerned with upland studies related to the lack of deep basins and the abundance of shallow blanket peat deposits with inherently poor temporal resolution, which frequently cover only short periods of time. The lack of radiocarbon dated pollen profiles hampers both inter-site correlation and the interpretation of the timing of significant events in the pollen record. Further problems are created by the destruction of the environmental archive through human activity during prehistoric and historic time e.g. peat cutting, drainage and mineral extraction operations (Caseldine and Maguire, 1981). Although there are problems with the nature of the evidence much valuable work has been conducted and will briefly be presented in the following paragraphs to place the site discussions in context. Discussion of the environmental history of south west England may be divided into two zones: the moorland areas, and the lowlands and coastal fringe (Fig. 2.2).

The moorland zone (Table 2.1)
The earliest palaeoecological evidence from organic sediments was found at Hawks Tor and Parsons Park on Bodmin Moor (Conolly et al., 1950; Brown, 1977; Caseldine, 1980). At both sites the Late-glacial vegetation was characterised by open grassland with a rich herbaceous flora. Ameliorating climatic conditions during the Late-glacial Interstadial are reflected at Hawks Tor by the development of Juniperus scrub and intense solifluction activity after ca. 12000 BP (ca. 10000 BC). Between ca. 11500 and 11000 BP these sites record the spread of scattered Betula trees probably in the lower valleys, forming small pockets of carr woodland. Sediments dating to the period of the Loch Lomond Stadial suggest an environment returning to periglacial conditions, in which woody components of the flora diminish and are replaced by grasses and sedges. The initiation of these colder conditions has been dated to 10884±210 BP (Q-1016) at Hawks Tor (Brown, 1977).

The earliest sediments encountered so far on Dartmoor date from the Loch Lomond Stadial ca. 11000-10000 BP, and are found at Blacklane Brook, near to the head of the River Erme (Simmons, 1962, 1964b; Simmons et al., 1983), and at Black Ridge Brook (Caseldine and Maguire, 1986; Caseldine et al., 1987). Both sites indicate the general absence of woodland in the area and the dominance of open ground plant communities, with a wide range of taxa indicative of arctic
Figure 2.2 Palaeoenvironmental and archaeological sites of south west England discussed in the text.
<table>
<thead>
<tr>
<th>Time</th>
<th>Cultural period</th>
<th>Activity</th>
<th>Evidence</th>
<th>Vegetation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD 1000 - 1600</td>
<td>Medieval</td>
<td>Tin streaming, peat cutting, limited arable cultivation, pastoralism. Settlement on lower fringes of the moor.</td>
<td>Extensive tin streaming remains throughout uplands of south west. Medieval long houses and associated features.</td>
<td>Open moorland dominates, with limited stands of Corylus, Betula and Quercus.</td>
</tr>
<tr>
<td>AD 400 - 1000</td>
<td>Dark Ages</td>
<td>Low scale pastoral activities.</td>
<td>No evidence for settlement on the moor at this time.</td>
<td>Largely open areas dominated by grasses and ericaceous species.</td>
</tr>
<tr>
<td>0 - AD 400</td>
<td>Romano-British</td>
<td>Limited use of moorland resources.</td>
<td>No archaeological evidence for human activity.</td>
<td>Pockets of woodland in unfavourable locations</td>
</tr>
<tr>
<td>500 BC - 0</td>
<td>Iron Age</td>
<td>Movement of people from moors to lowlands. Possible grazing activity - transhumance.</td>
<td>Lack of settlement evidence for all upland areas in south west. Evidence in lowlands include hillfort and pallisaded structures.</td>
<td>Regrowth of blanket bogs under deteriorating climatic conditions.</td>
</tr>
<tr>
<td></td>
<td>Late</td>
<td>Increased deforestation, cultivation, construction of large settlements and complex ritual monuments. Reaves.</td>
<td>Diversity of settlement types: single hut; hut villages; huts.</td>
<td>Mosaic of woodland patches, moorland, grassland. Intense grazing activity</td>
</tr>
<tr>
<td></td>
<td>Mid</td>
<td>Deforestation, increasing settlement activity on the moors. Increased cultivation activity.</td>
<td>Round barrows, single inhumations. 'Beaker' period - pottery.</td>
<td>First significant incursion to upland woodlands. Expansion of ruderal species and arable weeds.</td>
</tr>
<tr>
<td>8000 - 3000 BC</td>
<td>Mesolithic</td>
<td>Small scale activity in forest - very limited evidence.</td>
<td>Flint scatters typically favouring spring head sites and caves.</td>
<td>Closing woodland cover. Maximum height of tree-line attained during this period.</td>
</tr>
</tbody>
</table>

Table 2.1 Human activity in the uplands of south west England during the Holocene.
conditions. Ameliorating climatic conditions on Dartmoor after ca. 10000 BP were marked by a reduction in herbaceous species and an increasing shrubby woodland component. It appears that the development of a woodland cover was delayed following the onset of Holocene conditions in relation to other upland areas of the British Isles. Numerous studies suggest thermophilous taxa such as *Betula* and *Corylus* spread rapidly through the country following deglaciation, occurring widely by ca. 9500 BP (Huntley and Birks, 1983; Huntley, 1993), but on the upland moors of the south west ericaceous heathland species were still present until 9000 BP. Caseldine and Maguire (1986: 262) accept that exposure may be a factor, as proposed by Brown (1977) for Bodmin Moor, but conclude:

"a combination of coarse-textured parent material, exposure and possibly the winter temperature regime could lie behind the persistence of open ground after the end of the [Loch Lomond] Stadial".

*Betula-Corylus* woodland eventually spread onto these upland areas by ca. 8000 BP. The environment after this time was composed of a subtle range of ecosystems with *Quercus* and *Corylus* rapidly forming the major components of the woodlands. After ca. 7000 BP *Alnus* invaded suitable sites, although it must be noted that the timing of invasion was not a synchronous event for Dartmoor (Chris Caseldine, *pers. comm.*), with a range of dates for different areas of the moor, as experienced for a number of other areas in the British Isles (e.g. Chambers and Price, 1985). A common precursor to invasion of *Alnus* in many areas was site disturbance (Bush and Hall, 1987; Chambers and Elliott, 1989). The woodlands of the south west at this time were composed of the three species mentioned with smaller quantities of *Betula, Pinus* with some *Fraxinus, Ulmus* and *Tilia* (Simmons, 1962; Caseldine and Maguire, 1981; Huntley and Birks, 1983; Maguire and Caseldine, 1985). The forest would have contained natural clearings with associated heliophytes, as suggested by Beckett (1981) for areas on Shaugh Moor in the lower southern area of Dartmoor. The moorland summits would have supported a community composed largely of ericaceous species with grasses, sedges, *Rumex* species and members of the Asteraceae family (Maguire and Caseldine, 1985).

The soils of this time would have been characterised by base rich brown earths in which nutrient cycles and soil micro and macro fauna were active supporting a diverse woodland cover (Findlay *et al.*, 1984). Following the first evidence for forest disturbance and the use of fire (Simmons, 1962, 1964a,b; Hatton, 1991; Caseldine and Hatton, 1993), in association with changing climatic conditions around 7000 BP, a number of different soil types evolved. At high altitudes and slopes
thin blanket peats (≤1m) developed. These soils had a slowly permeable A horizon resulting in peaty gley soils, with restricted development of peaty gley podzols (Staines, 1974). This period marked the development of many of the valley bogs on Dartmoor due to a multiplicity of triggering factors, including increased precipitation rates, deforestation of slopes increasing water yields, and increased build up of acidic humic material (Clayden and Manley, 1964; Maguire, 1983). Clearance of the forest cover would have resulted in the subsequent development of acid grassland and accompanying acidification of brown earth soils, with low tree regeneration rates as experienced at Pinswell (Hatton, 1991; Caseldine and Hatton, 1993). It seems likely that these processes were under way by Neolithic times in the uplands of the south west. The fragmentary evidence from the lowland areas suggests the soils were still relatively nutrient rich and supported a dense woodland cover. The major differentiation of soil types occurred after the Neolithic Ulmus decline of ca. 5000 BP, with peaty gleyed soils of the Hexworthy group becoming dominant on gentle slopes. These formed the dominant moorland soil which characteristically contained a thin iron pan at ca. 15cm, overlain by an acidic loam unit, over which a thin peat layer developed.

In the following millennia the uplands of the south west saw much disturbance which began during late Mesolithic and Neolithic times, and culminated in the active settlement and utilisation of moorland resources during the mid and late Bronze Age periods. A somewhat different picture emerges for Exmoor since The Chains and Hoar Tor areas remained wooded until Neolithic times (Merryfield and Moore, 1974) with high Quercus pollen values before 4170±75 BP (UB-821). The lack of palaeoenvironmental studies from this upland hampers discussion of general vegetational trends, which forms a major gap in the palaeoenvironmental database for south west England (Straker and Crabtree, 1995), although the work of Francis and Slater (1990, 1992) on Hoar and Codsend Moor has extended the knowledge of environmental development from mid-Holocene times in this small area of Exmoor.

Significant incursions of the high level woodlands were made during the Bronze Age resulting in large scale conversion of these areas to acidic grass and heathland (Beckett, 1981; Hatton, 1991; Caseldine and Hatton, 1993), with only marginal woodlands in unfavourable situations (e.g. Barkham, 1978). Reduction of the woodland cover was accompanied by evidence for a shift in the nature of moorland utilisation, with organised pastoral activities associated with the construction of large scale boundaries (reaves) on Dartmoor around 3600 BP (Fleming, 1988). Evidence for cereal
cultivation associated with a number of settlement sites has been detected, particularly around the lower fringes of the moor on Shaugh Moor (Beckett, 1981) and Holne Moor (Maguire et al., 1983). Similar events have been observed from this period on Bodmin Moor (Gearey, 1996; Gearey and Charman 1996).

The vegetation of the uplands was largely in its modern form by the start of historic times. Discussion of the changes in the context of the results from some of the sites in this study further elucidates activities throughout this period, a time for which the palaeoenvironmental record from the peninsula is fragmentary (Caseldine and Hatton, 1996).

The lowlands and coastal areas

This zone of land is by far the most extensive in south west England, and accounts for approximately 60% of the total land cover. Little is generally known of the palaeoenvironmental conditions of this area. Studies of sea level change have been conducted on a number of coastal peat deposits and submerged forests in the coastal fringe (Hawkins, 1971a,b; Kidson and Heyworth, 1973) with emphasis placed upon 14C determinations of inter-tidal organic sediments from such sites as Start Bay and Hallsand in south Devon, and Penzance and Praa Sands in Cornwall (Heyworth and Kidson, 1982). Indeed coastal work has often provided the focus of interest in the lowland zone. Sand dunes are particularly important since they frequently seal former land surfaces and contain archaeological sequences interstratified with blown sand e.g. Gwithian (Megaw, 1976) and Harlyn Bay (Whimster, 1977) in Cornwall, Bantham in south Devon (Silvester, 1981) and Westward Ho! on the east Devon coast (Rogers, 1946; Balaam et al., 1987).

Another focus for palaeoenvironmental research in the coastal zone is provided in embayment environments. These features frequently developed during the mid-Holocene period under the influence of a relative sea-level rise in a sediment rich environment (Healy, 1996a). Records from such areas have produced important information about the changing coastline of the south west and the increasing influence of anthropogenic inputs to these systems. Published work on such sites includes Church Cove, Gunwalloe (French, 1996), Ponsandane (James, 1990), Marazion Marsh and Hayle Copperhouse (Healy, 1996b) and Looe Pool (O'Sullivan et al., 1982), in Cornwall, while in other regions of the south west similar sites are found at Slapton Ley (Crabtree and Round, 1967; O'Sullivan, 1994, 1996) and Porlock Bay (Canti et al., 1996; Jennings and Orford, 1996).
The palaeoenvironmental evidence from sites inland is often associated with the excavation of archaeological structures. Thus the driving force for reconstruction work in these areas is somewhat different from the stimuli for reconstruction of past environmental conditions in the uplands. Work in the lowlands has largely sought to place the local archaeology in its immediate geographical and temporal palaeoenvironmental context. This stems largely from the fact that suitable deposits were generally considered not to be present in the lowlands, and reconstruction has usually concentrated on soil pollen and micro-morphological analyses of sediments associated with ‘rescue-archaeological’ excavations, e.g. Colliford Reservoir (Caseldine and Maltby, 1980; Maltby and Caseldine, 1982; Griffith et al., 1984), and field systems of the Penwith Peninsula at Zennor (Herring et al., 1993).

The nature of evidence from the lowlands of south west England has produced a somewhat fragmentary picture of Holocene environmental change. The sites, although relatively numerous, lend little to the overall reconstruction. Clearly the absence of long sedimentary sequences is a problem in these areas, but with careful fieldwork and a degree of luck suitable deposits can be identified and provide essential data on the nature and scale of palaeoenvironmental conditions (Burton and Charman, in press).

2.1.3 Archaeology of the south west

Wainwright and Smith (1979: 132) state “the 500 square kilometres of Dartmoor contain what is probably the most impressive surviving prehistoric landscape to be found in Britain”. The importance of the archaeological remains of the uplands of the south west is evident, although the legacy of human settlement began long before the start of the Holocene. The earliest evidence for human occupation of the area dates to the Lower Palaeolithic period, a time when Britain formed part of a large peninsula of the European land-mass (Todd, 1987). Sediments from Kent’s Cavern, Torbay, contain a range of fauna including Ursus deningeri (bear) and artefacts relating to Acheulian industries (Todd, 1987; Proctor, 1996). Other sediments in the caves contain evidence for Middle and Upper Palaeolithic activity, as do caves from the nearby Torbryan Valley (Roberts, 1996). Sporadic finds in Cornwall relate to activity from this period, e.g. a small ovate chert handaxe from the Lizard, and an Acheulian handaxe from St. Buryan (Berridge and Roberts, 1986). Similar finds of Lower Palaeolithic Acheulian type implements have also been made in Porlock Bay and Doniford, north Devon (Grinsell, 1970).
Evidence for Mesolithic activity is represented in a number of sites in the south west. A concentration of Later Mesolithic artefacts was located on the northern fringes of Dartmoor at East Week (Greig and Rankine, 1953), and slightly further away in the area around Nether Exe, 7km north of Exeter (Silvester et al., 1987). Both sites contain evidence for an important Mesolithic flint tool industry, with a wide range of microliths represented. A similar site has been described around the shores of Dozmary Pool on Bodmin Moor which contains the largest potential assemblage of early Holocene microliths in the south west (Jacobi, 1979). Hawkcombe Head on Porlock Common features as a significant Mesolithic site which has produced a varied range of microliths (Grinsell, 1970). Further examples are located from lowland sites in the South Hams, mainly concentrated in coastal locations, including Burgh Island, Thurlestone, Bolt Tail, Soar Mill Cove and Bolt Head (Born, 1986). Most locations display a great variety of flint and chert implements consisting of scrapers, choppers, arrow-heads, knives and blades, which suggest both domestic and hunting activities. Artefacts indicative of largely domestic activity were discovered from a Mesolithic shell midden at Westward Ho! on the north Devon coast (Balaam et al., 1987).

Early hunting on Dartmoor is suggested by isolated microlithic finds at Huccaby, Postbridge and Yes Tor (Jacobi, 1979). A common feature of these assemblages is the representation of Neolithic technologies alongside Mesolithic artefacts, indicating a continuity of use at selected sites (Jacobi, 1979). The people of this time would have utilised a range of different habitats, both for food and raw material procurement. The summit moorlands and dense climax forests would have provided hunting areas for large mammals (Simmons, 1975), whilst the woodland edge could have produced supplies of wild berries and hazel nuts. The latter are known to have been an important foodstuff for the people of this period (Smith, 1970; Berridge and Roberts, 1986; Zvelebil, 1994). Indeed there is much speculation as to Mesolithic populations encouraging the growth of this species by the selective use of fire (Smith, 1970). Eustatic changes in sea-level during this period would have created significant inter-tidal habitats far inland, the biological diversity of which would have presented a rich opportunity for subsistence gatherers and fishermen (Simmons, 1975).

The results from pollen and charcoal analysis of deposits covering this period suggest the population were actively using fire as a forest management tool around Blacklane Brook (Simmons, 1962; Simmons et al., 1983), Postbridge (Simmons, 1964b; Caseldine and Hatton, 1996), and at Pinswell and Black Ridge Brook on the higher northern area of Dartmoor (Hatton, 1991; Caseldine and
Hatton, 1993). However, there is as yet no evidence for activity on other parts of the moor throughout the Mesolithic, including Blacka Brook (Beckett, 1981). The available evidence therefore suggests that the effect was only local and that regeneration of woodland generally followed clearance episodes, although a more significant effect may have occurred at forest edge ecotones in which the environment was considerably finer balanced (Smith, 1970).

Although there is a general lack of archaeological and palaeoenvironmental information about the hunter-gatherers who lived in the south west during the Mesolithic (Caseldine, 1980; Berridge and Roberts, 1986), the available evidence suggests valleys, particularly around the margins of spring heads, formed the major focus of exploitation, with transitory settlement in the immediate locality, e.g. East Week (Greig and Rankine, 1953) and Hawkcombe Head (Grinsell, 1970).

The division between the Mesolithic and Neolithic periods is classically cited in palaeoecological literature, as the period marked by the *Ulmus* decline. This horizon may be traced throughout north western European pollen diagrams, and is present, but difficult to detect around 5000 BP in south west England (Huntley and Birks, 1983; Birks, 1989). Almost concurrent with this decline in the pollen record is the appearance of a number of ruderal species, specifically attributed to anthropogenic disturbance activities (Behre, 1981). This suggests the population was engaged in woodland resource management and modification to allow agricultural practices to proceed, often with resultant soil degradation episodes and retrogressive forest succession (Iversen, 1964).

Another feature used to define Neolithic cultures is the introduction of pottery in the archaeological record. A number of distinctive forms developed and are useful in ascribing trade and communication routes based on typological differentiation of forms. A significant industry was present in Cornwall which displayed mainly examples of gabbroic ware, later taken as the major ceramic form of the south west. This was uninspiringly termed the ‘South-western style’, and was present at many sites including the important centre at Carn Brea which supplied ceramic materials for sites up to 27km distant between ca. 3000 and 2700 BC (Mercer, 1986). These sites included the important enclosed settlement at Helman Tor, near Lanlivery, Cornwall.

There are relatively few firmly dated Neolithic sites in south west England, but on the basis of structure and ceramic typology a number of settlements are attributed to this period including Carn
Brea, Helman Tor and Rough Tor in Cornwall (Mercer, 1986), with Haldon Hill and Hembury among the best examples in Devon (Pearce, 1978). These sites are commonly located on hill tops near to the upland fringe, although there is no unequivocal archaeological evidence for Neolithic settlement on the high moors of the peninsula (Radford, 1952; Hamond, 1979). The concentration of sites in these elevated localities is likely to be a function of destruction of archaeological remains in the lowlands following agricultural intensification during the historic period. However, recently a number of possible Neolithic earthworks have been identified by systematic survey in these lower lying regions. In particular a possible palisaded structure at Barcelona Farm, near Looe has been located (Keith Ray, pers. comm.).

A number of megalithic funerary monuments have been attributed to this period. They are generally located in the highland zone and all share a central chamber covered by an earthen barrow or stone cairn. Pearce (1978) suggests they are the lowland equivalent to the earthen long barrow. Particular examples exist around the south western edge of Dartmoor including Corringdon Ball and Cuckoo Ball, and on the north eastern flank of the upland at Spinster's Rock (Pearce, 1978). It is suggested that this group belongs to a wider geographic assemblage stretching westwards to Ireland, to the east throughout north western Europe and south to Brittany. Other monuments of this period include the impressive stone circles of Cornwall. Mercer (1986: 61) states them to display “perhaps the greatest variety ...... in any region of equivalent size in the British Isles”. These structures fall into two discrete morphological groups: those of Bodmin Moor, which include Stannon and Fernacre; and the group of the west Penwith peninsula. The henges of Cornwall at Castilly and Castlewich similarly may be placed in this time period, a time which saw the construction of the impressive ritual monuments of the Avebury area (Malone, 1990), as may a possible henge monument discussed by Grinsell (1970) on Parracombe Common, eastern Exmoor. The general sparsity of monuments in Devon during this time, except for the megalithic remains briefly described above may relate to destruction during the historic period. However, the lack of firm dating evidence of the numerous and extensive system of stone rows in the county, particularly on the Dartmoor granite, led Emmett (1979: 107) to conclude that “construction, extension and abandonment of the stone rows occurred between the Late Mesolithic clearances and the later Bronze Age”.

The Bronze Age, a period spanning approximately 2000 years between the last centuries of the 3rd millennium to ca. 900 BC (4500-2800 BP; Godwin, 1975), is characterised by dramatic
developments in technology, both in terms of ceramic and metallurgical wares throughout north western Europe. This period may be divided into a number of sub-periods (early, mid and late) on the basis of subtle changes in the style and character of archaeological material. The onset of this period is particularly well represented by the appearance of so-called 'Beaker' style pottery, which is found throughout the southern regions of Britain. These people had a developed set of religious customs which resulted in the construction of numerous round barrows with single inhumations, typical of the early Bronze Age, away from the multiple funerary long barrows of the earlier Neolithic period (Pearce, 1978). Although in Cornwall there exists a number of chambered tombs, suggesting a continuation of ancient traditions in this marginal area. There is no direct evidence of Beaker settlement in the south west, which may relate to the flimsy nature of early constructions, composed generally of a sheltered hearth with a number of pits, since it appears these people still favoured a partly nomadic lifestyle.

The middle and late Bronze Age is characterised by the construction of highly complex ritual monuments and by the recognition of Trevisker-style pottery, generally dated to the 13th century BC (Silvester, 1979; Christie, 1986). It is suggested that oak woodland was still present on the peninsula, particularly in the lower areas and on the steeper valley slopes (Todd, 1987). The woodlands of the upland were already beginning to suffer from human intervention, and the extension of moorland areas is notable during this period (Simmons, 1964a; Caseldine and Maguire, 1981). Extensive settlement evidence exists for these later periods, particularly well represented in the upland zones of Dartmoor (Butler, 1991, 1993; Price, 1993) and Bodmin Moor (Johnson and Rose, 1994; Gearey, 1996). Settlement appears to have taken three major forms (Hamond, 1979). Firstly, the single round hut, typically found on Dean Moor on the south eastern flank of Dartmoor. Secondly, clusters of huts forming a small village, with associated field systems. These are located in the western regions of the moor in the catchments of the rivers Tavy, Walkham and Meavy (Butler, 1991). Thirdly, the pound type settlement, composed of a number of huts enclosed by a dry-stone wall. Frequently these display evidence of animal pens and enclosures within the outer wall. On the basis of the archaeological remains it is possible to suggest that the first two groups were primarily concerned with mixed farming practices, while the pound type largely related to pastoral activities (Hamond, 1979; Price, 1993). Another striking feature of this mid to late Bronze Age period is the construction of what are locally known as 'reaves', substantial boundaries which divide large tracts of the upland into smaller territorial regions (Fleming, 1978a, 1988). These structures divide the
major river valleys into discrete landscape units. The lower areas are characterised by parallel reave systems probably used for crop production, with the upper zones divided into territorial grazing areas, each with access to the highest areas of common land. It is suggested that the construction of these structures dates to 1700-1600 BC and is a result of increasing pressure on upland resources (Fleming, 1979).

The most noticeable features of the upland landscape are the impressive ritual monuments which exist in both Cornwall (Christie, 1986; Johnson and Rose, 1994) and Devon, particularly on the Dartmoor upland (Brailsford, 1938; Emmett, 1979). These are too numerous to describe in detail, but generally include extensive stone alignments and rows, stone circles, cists and cairns. On the basis of typology they appear to date to the early to mid Bronze Age (Radford, 1952; Silvester, 1979; Fleming, 1988). This was a period of increased upland settlement which resulted in reduced woodland resources and the conversion of extensive areas to acidic grassland (Caseldine and Hatton, 1993). However, it is extremely difficult to place a firm date for the construction of these monuments since few have been thoroughly excavated, and almost none are associated with radiocarbon dates.

A significant feature of the Bronze Age was the advent of new metallurgical technologies. Price (1993) comments on the frequent relationship between habitation sites and the evidence for alluvial tinworking. Numerous examples exist in which archaeological artefacts have been located alongside evidence for prehistoric metal working. At Trevisker, Cornwall, cassiterite pebbles were located with evidence for on-site bronze working (ApSimon and Greenfield, 1972; Shell, 1978; Christie, 1986). Another site was discovered during excavation of a 17th century tin processing plant in the upper reaches of the River Walkham catchment (Gerrard and Greeves, 1992, 1993; Greeves, 1994). Here an amount of tin slag was found associated with prehistoric flints (Greeves and Newman, 1996). The major question is whether this evidence for early bronze working utilised the supplies of local cassiterite bearing river gravels as a source of tin (Charles, 1975). Recent work has suggested Ireland to have been an unlikely source for the tin (Budd et al., 1992; Budd et al., 1994), although northern France and central Europe had viable supplies at this time (Pearce, 1979). Support for the theory that the mineral deposits of south west England provided the tin for this early metal working is presented by Todd (1987), who describes Bronze Age objects found in alluvial cassiterite deposits. Clearly this question is one which deserves a great deal more attention in the future.
The transition to Iron Age times is marked by a postulated climatic downturn around 2700 BP (Godwin, 1975; Kilian et al., 1995). It appears that the uplands at this time were largely abandoned due to a number of different factors including the increasingly harsh environment, the spread of blanket bog and heathland, and the depleted natural resources. The population shifted to the lower fringes of the moors and the lowland zone. A settlement at Kes Tor, Dartmoor is almost the only example of Iron Age activity on the moor. Certainly after ca. 2300 BP there is no evidence for settlement in the Dartmoor area (Barber, 1977), and little evidence for Iron Age communities on Exmoor (Grinsell, 1970). Throughout the lowland at this time spread a people typified by a different style of ceramic ware, with curvilinear decoration, best known for its occurrence at the lake villages of Glastonbury and Meare in Somerset (Storer, 1985).

The change to Iron Age times is again marked by a different type of settlement in south west England. Morphologically similar to the enclosed settlements of the Bronze Age in the uplands, they were now characterised by 'rounds', which are said to have been the settlements of landowning kindred groups, while more elaborate multiple enclosure hillforts were occupied by the upper social stratum of chiefs (Quinnell, 1986). Excavation of Iron Age structures at Carn Euny, Cornwall, have revealed that the site was surrounded by open land used largely for arable cultivation, although this was initially cleared to provide pastoral land for grazing animals (Christie, 1978).

Little is known of the activities of the Roman legions in the south west, indeed it is possible they would have utilised the natural metal resources of the peninsula, but may have met considerable resistance from the Celtic people of the Dumnonii (Todd, 1987). By this time the uplands of the south west would be largely open with only isolated wooded areas.

During the Dark Ages there is no evidence for settlement from the uplands of the south west, however the more recent pollen analytical work suggests the possibility that these areas were utilised as a pastoral resource (Gearey, 1996).

Settlement activity on the upland moors occurs during the Medieval period, although there is no archaeological evidence to suggest Medieval habitation prior to AD 1200 (Allan, 1996; Henderson and Weddell, 1996). The settlement would have been associated with grazing activity, possibly seasonally, with small areas devoted to cereal production (Austin and Walker, 1985; Gearey and
Charman, 1996) characterised by ridge and furrow techniques (Austin et al., 1980; Fleming, 1996). The Medieval long house settlements characterise the main type of habitation (Beresford, 1979; Preston-Jones and Rose, 1986). This period saw the major episode of tinning activity in the uplands of the south west (Gerrard, 1996). Documentary evidence exists for workings at Whiteworks near Princetown which began operations in AD 1150. The scale of activity was largely governed by the price and subsequent demand for tin (Greeves, 1985). This period was therefore a very volatile period for settlement on the uplands, with an exodus occurring from Dartmoor during the mid 14th century AD.

A significant development in the tin industry came with the introduction of blowing houses and mills in the early 14th century. This allowed a more efficient smelt, resulting in the production of a much purer end product (Harris, 1992). Numerous examples are found on the uplands of the south west, particularly Dartmoor and Exmoor, the only requirement being a location close to a supply of flowing water. The development of these tanners' mills, was accompanied by the implementation of a network of leats capable of drawing water for tinworking activities. A further insight to the significance of Dartmoor's mineral wealth resulted in the appointment of Tavistock, Ashburton and Chagford as stannary towns in 1305.

After the high level activity of the Medieval period and early sixteenth century much quieter times followed during which tin mining took a role of lesser importance. The last major period of activity occurred during the 19th century. The Industrial Revolution encouraged prospectors to once again probe the moorland resources, now concentrating primarily on shaft mining, e.g. Whiteworks, Vitifer and Hexworthy Mines. However, this was never as economically productive as the exploitation of the alluvial tin deposits due to the problems caused by flooding, and the need for more thorough separation of tin from associated gangue minerals (Harris, 1992).

2.2 Field sites (see Fig 2.3)

The study sites for this investigation were carefully selected to address specific research issues concerning the Holocene of south west England. A unifying theme throughout the work was the assessment of EDMA in providing interpretable data, and the effectiveness of the technique in a range of sedimentary systems. Particular importance was placed upon the detection of signals indicating mineral extraction processes, deforestation episodes and acidification of catchment soils.
Fig 2.3  Field sites in south west England
2.2.1 North Sands, near Salcombe, south Devon (SX 730383)

The site is an infilled valley which has developed behind a bar feature. Borehole data from South West Water suggest the presence of unconsolidated sediments to a depth of ca. 16m. Sediments at this site have been accumulating from the mid-Holocene and are characterised by silty clays overlaid by ca. 8m of organic material.

The sediments from North Sands extend our knowledge of Holocene palaeoenvironments for this part of the coast. It was hoped the site would elucidate the geochemical signals associated with a marine to freshwater transition. Once terrestrialised the embayed area accumulates palaeoecological information relating to the immediate hinterland, and was hoped to provide cultural indications of the activities of the communities in the valley.

Further analysis of the sediments was carried out as a pilot study to test the general comparability of the EDMA technique to standard geochemical methods used in palaeoenvironmental reconstructions (Bengtsson and Enell, 1986).

2.2.2 Tor Royal, central Dartmoor (SX 602728)

Preliminary depth probing of Tor Royal revealed deposits in excess of 6m and suggested this site could provide an opportunity to investigate a long, high resolution Holocene sequence of palaeoenvironmental conditions from a central location on Dartmoor. It is possibly the last remaining raised mire on Dartmoor and contains the most extensive depth of sediment known from the upland. Thus it has the potential to solve some of the common problems of palaeoenvironmental research on Dartmoor (Caseldine, 1983; Caseldine and Hatton, 1996), which include poor temporal resolution and a lack of continuity in the record, particularly during Bronze Age and post Iron Age times.

Ombrotrophic sediments contain a regional signal of palaeoenvironmental change (Jacobson and Bradshaw, 1981) as they depend entirely on atmospheric supply of water and nutrients. This means that the sediments should contain inputs from aerial pollution, as well as a small contribution of locally derived wind-blown material. It was hoped the sediments would contain a record of pollution episodes from such activities as tin processing and other industrial activities. In addition, particular importance was placed upon the investigation of diminishing moorland resources through the Bronze Age and into the Iron Age, a period when it is largely assumed, due to the absence of archaeological
2.2.3 Upper Merrivale, River Walkham, west Dartmoor (SX 552766)

This site is a small flush fed mire in the upper reaches of the River Walkham catchment. The soligenous nature of the peatland system means the sediment contains material from a variety of sources, including mineral and organic material from the surrounding rocks and soils, and autogenic material from the developing peatland system. In contrast to Tor Royal the principal geochemical input is from immediate catchment sources rather than regional atmospheric sources. This case study thus sought to examine the potential use of EDMA in another sedimentary context.

The site is located close to an excavation of a 17th century tin blowing and stamping mill (Gerrard and Greeves, 1992, 1993; Greeves, 1994) which contains fragmentary archaeological evidence for earlier working at the site (Greeves and Newman, 1996). It was hoped the signals associated with this activity and would be recorded in the sediments and thus provide firm evidence for early human activity in the area and a valuable insight into the timing of activity and subsequent environmental disturbance.

2.2.4 Piles Copse, River Erme, south Dartmoor (SX 645623)

This site is in a similar situation to the site at Merrivale, in the upper reaches of an upland river catchment, surrounded by a concentration of industrial archaeology connected to the Medieval and post-Medieval period (Harris, 1992; Butler, 1993).

In addition the site lies very close to a proposed remnant of the mid-Holocene woodlands, one of the pockets of high level oak woods to have survived along with Black Tor Copse and Wistman's Wood. A further focus was therefore to investigate the antiquity of the woodland in comparison with work conducted in the area over 10 years ago (Roberts, 1983; Roberts and Gilbertson, 1994) which suggested periods of deforestation at unspecified times in the past.

Multiple cores were also used to address the problem of differential retention of geochemical signals in different sedimentary environments within a similar palaeoenvironmental context since one core (PC1) was obtained from a small flush fed hollow, while the other (PC2) was taken from an area of blanket bog.
2.2.5 Crift Down, near Lanlivery, Cornwall (SX 067596)

The site is a lowland mire and in a different environmental setting to the sites introduced so far. It is remote from the intrusive granitic rocks, but still in the metamorphic aureole associated with this activity.

A significant feature of the local landscape is the concentration of industrial archaeology indicative of mineral extraction and processing. A nearby Medieval smelting site is currently the focus of excavation (McDonnell, 1993; 1994). It was hoped that the signals associated with activity at this site would be reflected in the geochemistry of the sediments, with the palynological data providing data relating to the nature and scale of utilisation of local woodland resources and farming activities during these periods of known activity.

2.3 Data collection and analysis

This short section will briefly introduce the initial sampling strategies adopted for the fieldsites. A section will describe field sampling procedures followed by strategies for both pollen and geochemical analyses. Brief discussion will be made of radiocarbon dating procedures before a short review of the use of multi-variate statistical techniques is presented.

2.3.1 Field sampling strategy

In the selection of sites for this project the primary criterion was that a variety of sedimentary sequences were obtained, which reflected different levels of both natural and human induced environmental change. All sites were carefully selected to ensure a range of different sedimentary types was included, and that a range of different palaeoenvironmental signals would be detected.

Where possible sites were depth probed in two perpendicular transects using Russian auger rods, and surveyed to ensure the deepest body of sediment was recovered. Surveying provided spatial control allowing subsequent re-sampling if this was necessary.

Identification of wholly representative areas is of the utmost importance in the selection of sites for palaeoenvironmental investigations. Jacobson and Bradshaw (1981) working primarily with sites for palaeovegetational studies suggest the selection of the investigation area essentially determines the
level of detail that can be resolved. In peatland ecosystems there are a number of important variables to be considered which affect the resolution of the data: (i) basin characteristics; (ii) sedimentation dynamics; and (iii) characteristics of the local environment. All of these were considered in the selection of suitable field sites.

All field sampling was undertaken using a standard Russian auger, with a chamber diameter of 5cm, and a length of 50cm. Samples were extruded from alternate boreholes to minimise contamination of consecutive samples (Lowe and Walker, 1997), into cut lengths of drain-pipe, wrapped in hydrocarbon free clingfilm and aluminium foil. The samples were then stored in a fridge at 4°C prior to sub-sampling in the laboratory.

2.3.2 Laboratory sampling strategy and analytical techniques

Initially all the cores were subsampled for pollen and geochemical analysis at coarse regular intervals of between 5 and 10cm, depending on the depth of the profile. Samples were taken for carbon analysis and ashing at the same intervals. Samples for pollen analysis were prepared using standard procedures outlined in Moore et al. (1991). Samples of 1cm³ were submitted to NaOH digestion to break up the sample matrix and dissolve humic materials, treated with HCl (where appropriate) to dissolve CaCO₃, and HF (where necessary) to remove SiO₂ from the sample, and finally subjected to acetolysis to remove cellulose. Once extracted, samples were stained using safranine and mounted in silicon oil. Spore tablets (Lycopodium spp.) of known concentration were added to the samples to allow pollen and spore concentration to be calculated (Stockmarr, 1971). Pollen nomenclature follows Bennett et al. (1994), while plant names follow Stace (1991). To enable a statistically viable pollen sum to be calculated a minimum of 300 pollen grains (Total Land Pollen - TLP) were counted for all samples (Rull, 1987).

The presence of microscopic charcoal fragments in pollen slides provides a record of past fire history for an area (Patterson et al., 1987). The charcoal content of all samples prepared for pollen analysis was therefore assessed using a simple count scheme which involved counting fragments passing a graticule at the same time as pollen counting was undertaken. Charcoal concentration was calculated using the marker spore method utilised for the calculation of pollen concentrations (Robinson, 1984). This very simple approach was chosen due to the time constraints of the project as a whole. Further work would develop the interpretation made of these results by trying to quantify more accurately the
changing levels of this material (Clark, 1982). There are potential problems created when counting microscopic charcoal fragments which have been subjected to the same chemical procedures required for the preparation of pollen slides (Clark, 1984), but the results produced provide a first approximation to the levels of charcoal in the sediments, and compare well with other documented charcoal profiles from contemporary sites from the Dartmoor upland.

Samples for EDMA were air-dried for ca. 72 hours, then ground using an agate pestle and mortar which was cleaned thoroughly between samples, and mounted as described in section 3.1.3.

Carbon analysis was undertaken separately from the EDMA operation since sample preparation for the latter required the coating of material with a fine layer of carbon to improve analytical efficiency. Samples were prepared for analysis by a Shimadzu TOC 5000 Total Organic Carbon Analyser equipped with a SSM-5000A solid sample module. The samples were initially dried at room temperature for ca. 72 hours prior to grinding and sieving through a 63μm sieve. Samples were then placed in an oven at 110°C for two hours to remove interstitial moisture. Material was weighed carefully (±0.0001g), placed in a 1cm³ sample holder, covered with ceramic fibres and placed into the sample carrier. Each sample was fired at 900°C. The data were produced as percentages of total weight analysed. An experimental error was calculated by analysing the same material four times; this resulted in a maximum error of ±1.25%. These errors may occur for two principal reasons: (i) the small amount of material analysed (≤ 150 mg) and the heterogeneous nature of peat, and (ii) instrumental errors producing a background level of interference. However, this method seems to give a more reliable indication of the organic content of sediment than loss-on-ignition techniques (Kevin Solman, pers. comm.).

Ashing of peat in a muffle furnace at 900°C for 8 hours provided a first approximation to the amount of mineral matter in the profile (Aaby, 1986). Results were expressed as a percentage of the initial dry weight. Caution must be taken when interpreting ashed peat values in terms of the varying proportion of mineral matter, particularly in the upper sediments since bio-elements (Ca, Mg, Si etc.) may contribute significantly to the ash fraction, thus inflating the actual mineral content of the peat (Bill Shotyk, pers. comm.). The results obtained are interpretable in a number of different ways. However, generally low values (<5-10%) are particularly indicative of ombrotrophic peat sediments (Sillanpää, 1972). Peat is technically defined as material containing no more than 25% by weight...
mineral matter (Andrejko et al., 1983). Material exceeding this value may be defined as organic sediment and is typified by soligenous/flushed soils which contain much mineral material from weathering of local soils and rocks.

2.3.3 Radiocarbon dating procedures

Radiocarbon dating was used to date significant events in the palaeoenvironmental history of all profiles. Levels were chosen on the basis of both significant palynological and geochemical signals. Both standard radiometric and AMS (Accelerator Mass Spectrometry) analyses were used. The decision between the application of each technique was made on the basis of the amount of sediment available and the apparent temporal resolution of the profile, using changes in the arboreal pollen spectra and total pollen concentration curves as indications of sediment accumulation rate.

Both techniques are described in detail by Aitken (1990), Bell and Walker (1992) and Lowe and Walker (1997). Standard radiometric techniques generally require 100g of wet organic sediment. Pre-treatment included acidifying (hot HCl) the material to remove carbonates and washing with alkali (NaOH) to eliminate organic acids. AMS techniques require much less sediment (ca. 100mg wet organic material) and only the fine sediment fraction was dated to avoid contamination due to root penetration from the upper levels.

All samples were taken according to the guidelines of Pilcher (1991). Measured \(^{14}\text{C}\) ages are normalised with respect to the level of isotopic fractionation to the base of \(^{13}\text{C}/^{12}\text{C} = -25\%\) for standard radiometric dates, and for calculated values when using AMS techniques, which are generally in the range \(^{13}\text{C}/^{12}\text{C} = -20\) to \(-32\%\) (Stuiver and Polach, 1977). This operation provides a 'conventional' \(^{14}\text{C}\) age which may be calibrated to calendar years. Calibration is undertaken to reduce the distortion of chronologies and interpretation due to the variations between calendar and radiocarbon ages, which is created primarily as a result of the variable flux of \(^{14}\text{C}\) production through time (Bartlein et al., 1995). The CALIB 3.0 program of the Quaternary Isotope Laboratory, University of Washington was used for the calibration procedures (Stuiver and Reimer, 1993) for all dates reported in this research. In the site descriptions all radiocarbon dates are quoted as calibrated two sigma calendrical dates BC/AD with respect to AD 1950. The following sections detail the selection and different dating techniques applied to each study site.
North Sands

Only one sample was submitted from this site from a wood fragment at the bottom of the profile (12.50m below ground surface). The sample was submitted to the NERC Radiocarbon Laboratory for AMS analysis.

Tor Royal

Samples for standard radiometric analysis were taken from the Tor Royal site due to the abundance of sediment, with a high temporal resolution resulting in a 10cm slice of sediment spanning only ca. 100 years. Six evenly spaced samples were dated. The upper three samples were sent to the NERC Radiocarbon Laboratory, whilst the lower three samples were submitted to Beta Analytic Inc. The evenly spaced samples and the apparently even sediment accumulation rate allow the construction of a reliable age-depth profile.

Merrivale, Piles Copse and Crift Down

Samples from these sites were submitted to Beta Analytic Inc. for AMS dating due to the low amount of sediment available and the apparent lower temporal resolution of these profiles. Single centimetre slices were taken (ca. 1.5g wet sediment) from the cores, with only the fine fraction utilised for dating procedures to reduce the possibilities of sample contamination from root penetration. Two samples were taken from both the Merrivale and the Crift Down profiles, with one sample taken from each profile from the Piles Copse material.

2.4 Data analysis

2.4.1 Profile zonation

Each profile presented has been divided into zones which display internally homogenous characteristics with respect to the other samples analysed (LPAZ - Local Pollen Assemblage Zone, and Chemizones). Each zone may be regarded as conforming to a particular set of environmental parameters. Each chemizone may be considered as a litho-facies representing a distinct sedimentary environment (Mannion, 1979; Grattan, 1994).

A range of different techniques were utilised for the zoning operations included within the ZONE program written by Steve Juggins, based upon the FORTRAN programs ZONATION, BARRIER and CONISS (Gordon and Birks, 1972; Birks and Gordon, 1985; Grimm, 1987). The final position
of the boundaries was determined using a combination of statistical analysis and operator experience.

2.4.2 Standard error bars
EDMA was based upon a number of separate analysis areas for each sample. The result expressed was therefore the average value for each element from the different analyses conducted (eight for each sample). Since a number of separate analysis areas are selected for a single sample and the mean used as a measure of the elemental composition of the sample, it was considered necessary to calculate standard errors of the mean (Shaw and Wheeler, 1994) as an indication of the homogeneity of the sample's composition. Since peat is a complex sediment composed of a variety of different materials, analysis of a number of sub-areas on a single carbon stub mounted specimen may produce unreliable results if only the mean composition of the sample is considered, since one analysis area may concentrate on a component of the sediment that is not generally representative of the sample as a whole. The use of standard error bars will thus act as an interpretation aid, pointing to samples in which one or more analyses have focused upon unrepresentative analysis areas.

2.4.3 Multi-variate statistical methods
These techniques have long been used in the fields of ecology as an aid to the description of plant communities at varying scales (Kent and Coker, 1992). The overall aims of using such procedures is to reveal environmental gradients operational within the data. Each individual in the analysis is positioned with respect to the level of similarity between other components in the data set. When grouping of individuals is evident each individual in each group is more similar to the other individuals in that group than to any other individual in any other group.

The application of these techniques by the palaeoecological community is still relatively rare. There is a supposition that the extra work rarely results in additional knowledge. However, due to the large volume of data produced in a study of this nature it was decided to use detrended correspondence analysis (DCA - Ter Braak, 1987) since this technique may be viewed as the "preferred method for analysing highly heterogeneous sets of samples in ..... palaeoecology" (Prentice, 1986: 783). For a review of the development of these techniques, and their potential uses in palaeoenvironmental work see Prentice (1980, 1986), and Hicks and Birks (1996).
2.5 **Summary**

This chapter presented the methodological aspects of the research, from a presentation of the archaeological and palaeoenvironmental conditions of south west England, which sought primarily to place each fieldsite in context, to a discussion of sampling and data analysis/presentation techniques. The next chapter describes in detail the major part of the methodological experimental work carried out during this project. This focuses upon the examination of different preparation techniques and the comparison of EDMA with respect to standard geochemical methods.
Chapter 3

Experimental procedures

3.0 Introduction

This chapter describes the experimental investigations undertaken to address the following questions:

(i) what is the most appropriate sample preparation technique for EDMA of organic soils and clay?

(ii) How do the results gained from EDMA compare to those produced using other geochemical methods?

3.1 Investigation of EDMA sample preparation methods

There have been only a few attempts to investigate the most reliable method of sample preparation for EDMA. Although the analytical technique has been applied in a range of different situations (Pyatt and Lacy, 1988; Grattan, 1994; Pyatt et al., 1995), the experimental preparation of sediments has largely remained unexamined. These studies all involved the mounting of ground sediment samples directly onto a SEM carbon stub, secured using graphite cement. It was considered appropriate to develop and examine other methods of sample preparation, including the one described above, as the first component of the experimental development of this technique.

Sample preparation for EDMA is a necessary operation for any X-ray technique. It is required specifically to:

(i) reduce the build up of charge on the specimen surface. This reduces the possibility of sample damage, since the high beam currents used can lead to rapid loss of organic material (Hall and Gupta, 1974), and possibly even elemental losses.

(ii) Remove moisture from the sample. This will improve analyser efficiency and reduce high vacuum pump down times considerably, subsequently reducing degassing effects (Goldstein et al., 1981). Sediments, such as peat, with a high moisture content present the greatest difficulties to the preparation procedure (Tovey and Wong, 1978).

(iii) Homogenise the sample. Due to the heterogeneous nature of the sediments under investigation the potential effects of bias will be reduced by sample homogenisation.

A good preparation will therefore aid matrix correction procedures (ZAF-4), and improve
quantitative accuracy. It is generally considered that polished flat surfaces should be used to obtain fully quantitative results (Erasmus, 1978; Goldstein et al., 1981) as used in mineralogical analysis of rock samples (Kiel and Fredriksson, 1964; Straszheim et al., 1988; Kwiecinska et al., 1992). However, given the friable nature of the sediment to be analysed, it is extremely difficult to obtain these conditions. A number of different methods were therefore investigated based on two general procedures, which sought to address the points outlined above:

(i) mounting the sample directly onto an SEM carbon stub, as described in Pyatt and Lacy (1988), Grattan (1994) and Pyatt et al. (1995), (referred to as methods A to C here).

(ii) embedding the specimen in resin and grinding flat. This was performed to obtain a level analysis surface (methods D and E).

Samples were taken at the following position from the North Sands core (see Chapter 4): 1.30, 3.30, 5.40, 7.50, 9.30, 11.40m, numbered 1 to 6 respectively. This ensured a range of different sedimentary units were investigated, from highly organic sediments to silty clays. It was decided to analyse each sample for: Na, K, Mg, Ca, Mn, Fe, Cu, As, Sn and Pb using samples prepared according to the procedures described in Table 3.1. These ten elements were chosen since they represent a range of different groups of chemical elements i.e. major, mobile and heavy metal elements. Ideally the full range of elements would have been investigated, including Si, Al, S and P, but this was not feasible at this early stage in the project.

Table 3.1 describes the specific operations of each method (A - E). In addition to the five preparation methods, standard bulk chemical extracts were made from material at the same depths, for the same elements to act as a comparison of the geochemistry of the samples, following the methods outlined in Bengtsson and Enell (1986). A combination of Atomic Absorption Spectrometry (Ca, Mg, Fe, Mn, Pb, Cu, As, Sn) and Flame Photometry (Na, K) were used. The bulk chemical data (ppm) were standardised to 100% so that they were directly comparable to the results from EDMA (the totals from which were ≥95%), and analysed using the Wilcoxon test for paired samples (Hammond and McCullagh, 1978; Matthews, 1981). This is a non-parametric test were the null hypothesis states that the two sets of data come from identical, equivalent populations (Hammond and McCullagh, 1978). The test considers not only the direction of the differences between pairs, but also the relative magnitude of these differences, giving more weight to a pair which shows a large difference between profiles than to a pair which shows a small difference (Siegel and Castellan, 1988). The main use of
All samples were air dried for 72 hours, then ground to a fine powder (ca. 63μm) using an agate pestle and mortar which was cleaned thoroughly with distilled water between samples.

**PROCEDURE 1**

Coat a carbon stub of 13mm diameter with graphite dag onto which the sample is peppered.

<table>
<thead>
<tr>
<th>Method</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Preparation as described in Pyatt and Lacy (1988), Pyatt et al. (1992) and Grattan (1994). The mounted sample was sprayed with Duron anti static solution.</td>
</tr>
<tr>
<td>B</td>
<td>Samples were placed in a low vacuum desiccator for 24 hours to remove interstitial moisture from the specimen, then sprayed with Duron.</td>
</tr>
<tr>
<td>C</td>
<td>The sample was coated with a layer of carbon in a vacuum evaporation unit, coating thickness is sufficient when a piece of filter paper placed on the stage turns a light chocolate brown colour.</td>
</tr>
</tbody>
</table>

**PROCEDURE 2**

The samples were embedded in epoxy resin (Spurr low viscosity), as suggested in Goldstein et al. (1981) and Erasmus (1978). The surface of the resin was ground down using silicon carbide paper until the sample was exposed. Using a frosted glass plate and silicon carbide slurries (600 grade for 25μm, followed by 302 grade for 11μm), each stub was ground down until a smooth, even, flat surface was attained (specimen micro-topography was examined using a low powered binocular microscope). Resin blanks were prepared, which were subjected to each stage of the preparation procedure to check for contamination from the resin (Cl and S are possibilities), and the addition of extraneous material from the grinding pastes.

<table>
<thead>
<tr>
<th>Method</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>The samples were placed in a low vacuum desiccator to remove air bubbles from the resin and interstitial moisture from the specimen matrix. The samples were then transferred to a low temperature oven (50°C for 24 hours) to allow the resin to polymerise. Ground, as described above, any contaminants were removed in an ultrasonic bath (de-ionised water, no detergent). The stubs were then placed in a vacuum desiccator unit for ca. 24 hours to remove moisture, and finally sprayed with Duron. The sides of the analysis surface, and the vertical edge of the stub were coated with graphite dag to ensure good electrical conductance between sample and holder.</td>
</tr>
<tr>
<td>E</td>
<td>As D, but the stub was coated with C in an evaporation unit after the ultrasonic cleaning operation.</td>
</tr>
</tbody>
</table>

Table 3.1  EDMA experimental preparation techniques
this technique is to assess the amount to which the profile features (peaks and troughs) produced by each preparation method are coincident with those of the bulk procedures, and therefore indicate the accuracy of the EDMA.

Standard errors of the mean were calculated for each sample to address the question of replicability between different analysis areas for the same sample for each preparation technique (Fig. 3.2a-e). All EDMA analyses were conducted with the microprobe operating conditions set as outlined in Table 3.2 below.

<table>
<thead>
<tr>
<th>Live time</th>
<th>100 seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dead time</td>
<td>&lt;25% at ca. 2500 counts per second</td>
</tr>
<tr>
<td>Magnification</td>
<td>x500</td>
</tr>
<tr>
<td>Accelerating voltage ($E_a$)</td>
<td>20 keV</td>
</tr>
<tr>
<td>Analyser</td>
<td>Link Analytical electron microscopy data management system (eXL), with an energy dispersive microprobe attached to a Joel 6100 SEM</td>
</tr>
<tr>
<td>Analysis</td>
<td>Each sample was analysed 8-10 times (randomly selected areas), the results were averaged and expressed as mean ±2 standard errors</td>
</tr>
</tbody>
</table>

Table 3.2   EDMA operating conditions

3.1.1 Discussion of the preparation techniques

All samples were initially air-dried, then ground to a fine powder as described in Table 3.1. The division between the two sets of preparation procedures relates to the specific method of sample mounting. Methods A to C were based upon the peppering techniques adopted by Pyatt et al. (1995) and Grattan (1994) for previous palaeoenvironmental studies. Methods D and E were based upon the resin embedded methods, commonly utilised for analysis of biological specimens (Erasmus, 1978).

The use of Duron, a polynene derived anti-static agent, may reduce specimen charging effects (Goldstein et al. 1981), and was consequently utilised in the development of methods A, B and D. An investigation undertaken by Pease and Bailey (1975) states that thin polymer films (1.2-20nm) are readily transparent and relatively stable under an incident electron beam. A 5.0nm coating of polymer has a number of advantages over other coating techniques: no special equipment is required for the coating operation; irregular surfaces may be coated; the method is cheap and rapid; the coat does not hinder light microscopical examination; and the film, having a low backscattering
coefficient results in the production of fewer secondary electrons.

The problems associated with interstitial water in the sample were addressed by placing the samples (methods B, C, D and E) in a vacuum desiccator unit prior to analysis to reduce sample degassing and high vacuum pump down times.

Methods C and E involved a layer of carbon evaporated on to the surface of the sample under a working vacuum of $10^{-4}$ Torr. This is an effective way to coat the sample to provide good electrical conductance, reducing charge accumulation on the specimen surface and the problems of thermal damage, sample movement and image distortion. Goldstein et al. (1981) suggest that organic samples may be fixed more firmly by applying a thin coating of carbon. This has the advantage of preventing loss of materials during analysis.

Embedding the specimens in resin was seen as an alternative to the methods described in procedure one since the variable surface geometry of samples may create problems for analysis. The surface should therefore be as flat as possible, which will aid the determination of concentrations of elements present in the sample. Erasmus (1978) states that embedding samples in resin will simplify the manipulation and sectioning of the specimen, but care must be taken when selecting embedding materials since some may contain high levels of elements that interfere with those of the analysis, e.g. Araldite is said to contain Cl and S (Davies and Erasmus, 1973). For this investigation Spurr low viscosity epoxy resin was considered suitable, and resin blanks were prepared to check for the presence of possible contaminants. Ideally a completely flat surface should be attained to maximise analyser efficiency, and would involve repeated polishing to less than 1μm with high quality diamond pastes, with ultrasonic cleaning between each polish (Kane, 1973; Hunt and Hill, 1993). It proved impractical to polish to this level due to the friable nature of the matrix under investigation. It was considered sufficient to grind the surface down to ca. 11μm, and utilise the fact that high take-off angles may be used to reduce the effects of local surface inclinations, produced by the grinding/sectioning procedure (Yakowitz and Heinrich (1969) suggest $\geq 45^\circ$). Preparation method E was undertaken since it was hoped to share the benefits of a flat analysis surface, with those of using carbon as a coating material.

Each method contained ten randomly selected analysis areas for each sample. A number of analysis
areas were analysed three times to assess reproducibility on the same analysis area.

In the following discussion a number of different physical criteria were assessed visually and used as an indication of the suitability of each method. These included an assessment of charging, i.e. how much of the incident electron beam was absorbed by the various parts of the sample. In extreme situations it results in the sample effectively becoming an 'electron mirror' (Roy Moate, pers. comm.), seriously effecting the production of characteristic X-rays and consequently reducing analytical efficiency. Sample movement is another criteria which essentially relates to how effectively the sample is fixed to the carbon stub, which is likely to vary for the different techniques. Contamination is shown as a build up of material in the focused area of the microprobe during recalibration of the instrument and is most likely to be a function of contamination of the vacuum creating this transient residue on the cobalt calibration stub.

3.1.2 Results

Method D failed since a residue formed on the analysis surface of the sample. This is probably due to interaction between the Duron and the epoxy resin. In a discussion of the results obtained from the remaining preparation techniques, a number of issues are important:

(i) the sample-analysis system interaction
(ii) the level of replicability within an individual analysis area
(iii) the absolute differences between the different techniques with respect to standard bulk geochemical operations
(iv) the replicability between analysis areas for the same sample.

Sample-analysis system interactions

One of the aims of a preparation technique is to minimise sample charging, movement and contamination since these may lead to spurious data and a reduction in analyser efficiency. The assessment of these criteria was subjective since it would have been impossible to quantify the interaction, each preparation method was described using a low-medium-high scale. Three of the methods (A, B, C) investigated did not seem to reduce these problems. However, method E was more successful (Table 3.3) and resulted in lower levels of charging and sample movement. There is no indication of how significantly these effects reduce the sensitivity of the machine, but it is obvious that their effects should be minimised wherever possible.
### Method A
- Charging: High
- Movement: Medium
- Contamination (build-up): High

### Method B
- Charging: High
- Movement: High
- Contamination (build-up): High

### Method C
- Charging: Medium
- Movement: High
- Contamination (build-up): High

### Method D
- Charging: Method failed

### Method E
- Charging: Low
- Movement: Low
- Contamination (build-up): Low

#### Table 3.3 Visual assessment of sample - analyser system interactions

**Replicability within an individual sample area**

One of the key issues with the development of any new technique is reliability of the analytical method. The use of identical operating conditions and frequent re-calibration of the analyser goes some way to ensuring constancy, but it is largely unknown how replicable EDMA analyses are. It was decided to answer this question by simply analysing a given area at ×500 magnification for 100 seconds live time, then repeating this procedure three times. The results for all methods are in the region of ±0.05% for the base and trace elements, and up to ±0.75% for the more abundant elements, such as Fe. This suggests that the results from analysis of individual areas for any one preparation technique are highly replicable, and there is no need for the replication of single analysis areas. However, this says nothing about the reliability and accuracy of each preparation technique.

**Absolute differences between the different techniques**

Since all EDMA analyses were conducted under the same operating conditions (Table 3.2) any variation between different preparation techniques with respect to bulk chemical results gives a reflection of the overall efficiency of the individual preparation technique. Wilcoxon test coefficients (Table 3.4) were calculated for techniques A, B, C and E in comparison to bulk results and illustrate the lower level of similarity between method E and standard chemical procedures, illustrated on Fig. 3.1a-e. This was probably due to the use of epoxy resin introducing elements which interfered with the analysis (Erasmus, 1978). The grinding procedures similarly added small quantities of Al and Si obscuring the chemical signatures of the samples. Methods A, B and C demonstrate a statistically significant level of similarity with standard chemical procedures for Na, K, Ca, Mg, Fe. There is inevitably a degree of inconsistency in the relationship due to the different ways in which the methods produce the data (Erasmus, 1978).
Replcatability between different analysis areas for the same sample

Figure 3.1a Na on left, K on right. Vertical axis indicates the percentage of the element in the analysed volume of the sample. X-axis displays the sample number, vertical bars show ±2 standard errors of the mean. All data are standardised to 100%.
Figure 3.1b  Mg on left, Ca on right. Vertical axis indicates the percentage of the element in the analysed volume of the sample. X-axis displays the sample number, vertical bars show ±2 standard errors of the mean. All data are standardised to 100%.
Replicability between different analysis areas for the same sample

Figure 3.1c  Fe on left, Mn on right. Vertical axis indicates the percentage of the element in the analysed volume of the sample. X-axis displays the sample number, vertical bars show ±2 standard errors of the mean. All data are standardised to 100%.
Replicability between different analysis areas for the same sample

Figure 3.1d  Pb on left, Cu on right. Vertical axis indicates the percentage of the element in the analysed volume of the sample. X-axis displays the sample number, vertical bars show ±2 standard errors of the mean. All data are standardised to 100%.
Replicability between different analysis areas for the same sample

![Graphs showing replicability](image)

Figure 3.1e  As on left, Sn on right. Vertical axis indicates the percentage of the element in the analysed volume of the sample. X-axis displays the sample number, vertical bars show ±2 standard errors of the mean. All data are standardised to 100%.
This point is illustrated by the general variations in the heavy metal elements. These elements exhibit
the lowest concentrations and are therefore the hardest to detect (Fig. 3.1d and e).

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Pb</th>
<th>As</th>
<th>Sn</th>
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<td>15</td>
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<td>21</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>10</td>
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</tr>
<tr>
<td>B</td>
<td>14</td>
<td>20</td>
<td>21</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>17</td>
<td>17</td>
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<tr>
<td>C</td>
<td>11</td>
<td>21</td>
<td>21</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>12</td>
<td>16</td>
<td></td>
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<tr>
<td>E</td>
<td>8</td>
<td>21</td>
<td>21</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>15</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4 Wilcoxon test statistic matrix for comparison between the geochemical data obtained from EDMA and standard analytical procedures for the different preparation methods investigated. It is possible to accept H₀ (no difference) at the 95% significance level if the tabulated value is greater than 0 (Matthews, 1981).

Statistically significant levels of consistency were exhibited in the analysis of the Na, K, Ca, Mg, Fe, Pb, As and Sn for preparations A, B and C with respect to bulk chemical procedures, with the plots of K, Ca and Fe for all of the preparation techniques illustrating similar results (Fig. 3.1a, b, c). The lack of similarity for Mn and Cu may be due to a number of factors including the detection capabilities and efficiency of the each analytical instrument. The trace elements were in low concentration (Cu range: 0.05-0.9ppm; Pb: 0.1-0.25ppm; As: 0.3-3.3ppm; Sn: 0-0.5ppm), approaching the detection limits of the AAS technique. This may partly explain the low levels of similarity between the data produced by the two techniques. A similar explanation for the rejection of H₀ for Mn may be suggested since this element is in concentrations of <5ppm. The extraction method used for the bulk procedures may have been incapable of releasing some elements to solution, reducing the level of similarity between EDMA and the bulk chemical methods. Further analysis is required to resolve this matter.

**Replicability between different analysis areas for the same sample**

This part of the investigation sought to identify the level of replicability between different analysis areas for the same sample. The selection of small analysis areas is a potentially hazardous operation due to the heterogeneous nature of peat. Investigations were therefore carried out for each analysis area of a sample to see if the results gained were representative of the sample as a whole (Fig. 3.2). The most consistently low standard errors for all elements were displayed by
Figure 3.2 Schematic representation of sample analysis areas for EDMA. Eight areas are analysed, the mean of these is taken as the representative geochemical signal of the sample.
method E (Fig. 3.1a-e), however, there was a weaker statistical relationship exhibited between the results from this method and those from the bulk chemical procedures (Table 3.4). Qualitative analysis of resin blanks using EDMA indicated the presence of S, whilst the grinding pastes contributed amounts of Al and Si. The results presented on Fig. 3.1a-e suggest that all methods are variable in their presentation of the geochemical signatures of the sediment. It appears that some methods are more reliable than others for certain elements, e.g. Ca was comparable to bulk values for all preparation methods (Fig. 3.1b), whilst methods A and B most accurately corresponded to the bulk results for Fe (Fig. 3.1c). The high standard errors for all methods in the analysis of sample three for Mn (Fig. 3.1c) suggests that the width of the error bars may relate to the heterogeneous nature of the sediment at this level: composed of black humified silty peat with much schistose material, therefore selection of small analysis areas with very different geochemical characteristics may reduce the reliability of any interpretation from this level.

3.1.3 Discussion

The method favoured at this stage is derived from procedure one, Table 3.2. It seems the most expedient method of preparation as it involves mounting the powdered sediment directly on to the surface of a SEM carbon stub. The resin embedded methods, whilst providing a suitable analysis surface, must be rejected due to the contribution of elements in the resin and during the grinding procedures which are of interest to the analysis of peat sediments. It has been illustrated that methods A, B and C produced the most reliable results, however, the use of Duron in the preparation procedure has been questioned since it is felt that this compound may contaminate the vacuum chamber of the microprobe column, and subsequently impair analyser efficiency (Roy Moate, pers. comm.). The preferred method of sample preparation in this project will therefore involve the use of carbon as a coating material. The use of graphite dag as a mounting medium will be replaced by double sided adhesive carbon pads. These will reduce the effects of sample movement and address some of the problems of charging since more of the sample will be in contact with the earthed sample holder.

The analysis of samples at x500 magnification may lead to bias in the data and large standard errors, particularly if the analysis area is not representative of the sample as a whole. Analysis should thus be conducted at a lower magnification of x100, which will produce an 'average' signature for the area investigated.
There appears to be no need for replication of individual analysis areas for samples, since there was no significant variation between consecutive analyses. However, the use of no less than eight analysis areas per sample produces statistically viable results. This will allow the interpretation of highly heterogeneous samples and aid interpretation.

3.2 Comparison of EDMA and bulk chemical methods

The overall objectives of this section are as follows:

(i) to assess whether EDMA provides data which are comparable with other geochemical methods. Although exact values cannot be easily compared, the overall trends in the data should be similar.

(ii) to examine if the EDMA technique provides reliable data. Many workers (Gulson and Lovering, 1968; Erasmus, 1978; Goldstein et al., 1981) state that flat analysis surfaces are a pre-requisite for accurate quantitative analysis. However, semi-quantitative results have been obtained from the analysis of ‘rough’ surfaces of sediment samples (see for example Pyatt and Lacy, 1988; Pyatt et al., 1991; Pyatt et al., 1992; Grattan, 1994; Charman et al., 1995; Pyatt et al., 1995). This pilot study seeks to examine whether the results produced are meaningful for palaeoenvironmental reconstruction work.

Thirty nine samples were prepared for EDMA using the revised preparation procedures, and for bulk chemical analysis as described above in section 3.1. The data from both methods are presented as raw elemental plots and as standardised data (Figs. 3.3, 3.4 and 3.5). The data are also presented as transformed plots, in which each elemental profile is manipulated to have a mean of zero (Fig. 3.6). This enabled direct comparison of profile features using the Wilcoxon test for paired samples, and provided a statistical index of similarity (Table 3.5).

3.2.1 Results

As already stated ten elements were selected for comparison:

Base elements: Na, K, Mg
Carbonate elements: Ca
Mobile elements: Fe, Mn
Heavy metal elements: Cu, Pb, Sn etc.
Figure 3.3  Comparison between bulk analyses (solid line - ppm) and EDMA (% with 2 s.e.) for Na, K and Mg. The right hand diagram illustrates the expression of both data sets as percentages (sum 100%).
Figure 3.4  Comparison between bulk analyses (solid line - ppm) and EDMA (% with 2 s.e.) for Ca, Fe and Mn. The right hand diagram illustrates the expression of both data sets as percentages (sum 100%).
Figure 3.5  Comparison between bulk analyses (solid line - ppm) and EDMA (% with 2 s.e.) for Cu, Pb, As and Sn. The right hand diagram illustrates the expression of both data sets as percentages (sum 100%).
Figure 3.6 The plots illustrate the transformed data used in the Wilcoxon analysis (each data set therefore sums to 100%, and has a mean of 0).
Na  K  Ca  Mg  Fe  Mn  Cu  Pb  As  Sn
328 315 316 308 299 351 373 349 385 367

Table 3.5 Wilcoxon test statistic values for comparison between EDMA data and that obtained using standard chemical procedures. Both data sets have been standardised to 100% and transformed so that the means of each set equal zero to allow direct analysis of coincident profile features. It is possible to accept $H_0$ (no difference) at the >95% significance level if the tabulated value exceeds 249 (Matthews, 1981).

Base and carbonate elements

Analysis of Na suggests a good deal of similarity between the two methods (Fig. 3.3, 3.6), confirmed by a statistically significant result from the Wilcoxon test (Table 3.5). Both techniques generally demonstrate higher amounts in the uppermost sediments, with the overall trends reasonably well replicated for each method.

Both Mg and K form a greater proportion of the sample than Na. The reasonably consistent standard errors for these elements suggests reliable analyses. The level of similarity between features of the profiles for K is good, with peaks detected by both methods at 4, 5.75, 9 and 12m. However the basal sample proved problematic since higher levels of K were detected by EDMA than bulk chemical methods. This may be attributable to the inefficiency of the chemical extraction used (HNO₃, HCl) where perhaps the extraction method could not liberate the tightly bound K from these predominantly phyllosilicate sediments derived from the local mica schist rocks. Standard error deviations for Mg increase up through the profile possibly indicating changing fluxes of Mg to the sedimentary system through time, particularly in the uppermost sediments, as shown by increased standard errors above 5m. However, the level of similarity between the methods is statistically significant.

Calcium was selected to represent the carbonate elements in this pilot study since it was likely to be a major component of the basal material. All plots indicate a good deal of similarity between adjacent profile features. Elevated levels in the basal 3m of the sediment are detected, with a close correspondence between other features in the remainder of the section (Fig. 3.6).

Mobile elements

Fe displays comparable trends with respect to the EDMA and bulk chemical techniques (Fig. 3.4,
3.6). Iron displays low, consistent standard errors suggesting high reproducibility of the EDMA technique, and detects the major profile features produced by the bulk analysis, resulting in a significant Wilcoxon test statistic. Mn, a much smaller component of the sediment, displays a fluctuating profile for both techniques. A number of samples exhibit large standard errors effectively obscuring the remainder of the EDMA data. Discrepancies between the results gained from the two methods for this element occur at a number of levels in the profile (2, 5 and 6.6m). This possibly questions the validity of the EDMA data for Mn from this site, although it could equally stem from a problem with the standard chemical procedure, since the element is in low concentration (≤5ppm). A problem may stem from the variable extraction efficiency of the digestion method used.

**Heavy metal elements**

These elements are the most difficult to detect in a sample since, by definition, they are usually the smallest components of the sediment body (Bengtsson and Enell, 1986; Alloway, 1995). Problems of detection will influence any geochemical study, with difficulties created by variable extraction efficiency compounded in the analysis of these elements using standard chemical procedures since these elements are bound with varying efficiency in different sedimentary situations.

It appears Sn was present close to the detection limits of AAS making direct comparison of profiles difficult. There are common features to the profiles for As, Sn and Pb from the EDMA results. They all exhibit similar standard errors through the profile, and share peaks and troughs at the same levels, albeit of different relative magnitudes. The plots for the heavy metal elements, both standardised percentage (Fig. 3.5) and transformed (Fig. 3.6) display the least convincing levels of similarity between the two analytical methods. This questions the utility of the signals from these elements since they are present in very low concentrations, perhaps below the lowest limit of detection (LLD) of the EDMA techniques. This problem will be addressed in the analysis of the other sites.

3.2.2 Discussion

Most of the data produced from EDMA of the sediment was comparable to that produced from the bulk chemical procedures. However, there were discrepancies between these two methods. The variable success with which the chemical extraction released the elements to solution from the different sedimentary units may have caused problems, for example, below 12m K may have been
bound too tightly for the extractant (HNO₃, HCl) to release it, while it was readily detected by the EDMA technique.

It is possible that too much emphasis may have been placed upon the accuracy of the standard chemical procedure, since a number of elements seemed to have been present in the sediment at or below the detection limits of the analytical devices used. This will obviously make direct comparison between the two methods problematic, but for the major, carbonate and mobile elements there does appear to have been a good deal of similarity, both graphically and statistically.

3.3 Conclusions

Energy Dispersive X-ray Micro Analysis has produced results that are generally comparable with the bulk chemical operations. Although a limited number of elements have been examined, the trends produced may be used to make palaeoenvironmental reconstructions on the same basis that has been established for standard bulk chemical analyses (Bengtsson and Enell, 1986). These results suggest EDMA to be most reliable for the more abundant elements present in the sediment, but suggests caution must be exercised in the interpretation of the elements present in lower concentrations i.e. the heavy metal elements and Mn.

The technique produced consistent data within each sample as shown by the small range of values from the standard error calculations for the majority of samples. It seems therefore that EDMA of 'rough' surfaces prepared according to the method described in section 3.1.2 produces reliable data from which environmental processes may be deduced. This will now be discussed with respect to a range of different sedimentary systems located in south west England, beginning with the investigation of a coastal mire with a variety of different sedimentary materials.
Chapter 4

North Sands pilot study

4.0 Introduction

This chapter describes results obtained from EDMA using the new preparation methods and procedures outlined in chapter three. EDMA and pollen analysis of the sediment from a coastal mire at North Sands, south Devon, revealed a detailed picture of palaeoenvironmental development for this area of the Kingsbridge Estuary. The first section introduces the physical and historical character of the area, followed by the discussion of the analytical results and palaeoenvironmental reconstruction.

4.1 North Sands and the Salcombe area (Fig. 4.1)

The sampling site (SX 730382) lies in the lower reaches of the North Sands combe, at a height of 2.61m above OD, approximately 100 metres from MHW. The site was of particular importance since it had the potential to test the efficiency of EDMA using a range of different sediments, hopefully revealing information relating to marine/freshwater phases, aquatic/terrestrial phases and autogenic processes, in addition to the disturbance activities associated with anthropogenic activity. The site will further reveal important palaeoenvironmental information about this lowland coastal environment, a zone for which there is generally very little known in the south west.

4.1.1 Geology and Geomorphology

The rocks of this area of south Devon are part of the Start Point Complex (Fig. 4.2). Ussher (1904) divided the rocks of this complex into two distinct groups: (i) the Green Schists - green hornblende and chlorite schists; and (ii) the Grey Schists - grey pelitic schists. Both groups are derived from altered Devonian rocks, with possible remnants of the Lower Palaeozoic land mass that have been brought into contact with the Lower Devonian rocks by faulting (Edmonds et al., 1975). The Green Schist group are composed primarily of altered basic lavas or sills, with the distinction between the two sub-groups made with respect to the dominant mineral within each grade (Durrance and Laming, 1982). The Grey Schists are formed from slate, siltstone and sandstone, have a simple mineralogy of quartz and muscovite with numerous accessory minerals, and are more susceptible to weathering (Born, 1986). The North Sands study site lies within an area classified by Ussher as alluvial sediments, bounded to the north and south by hornblendic and chloritic schists.
Figure 4.1  North Sands and Salcombe
Figure 4.2  The geology around Salcombe (inset indicates area covered by Fig. 4.1)
The coastal plateau of this part of south Devon consists of a number of wide step-like terraces, the highest at around 240m OD on the fringes of Dartmoor, with the lowest at 60m in the area around Berry Head (Millward and Robinson, 1971). Each terrace was formed when the sea was at a higher level than at present. A number of rivers have subsequently cut down into these erosion surfaces during periods of lower sea-level forming the characteristic rias or flooded valleys of south west England, which were inundated by the rapidly rising sea level around 7000 years BP (Hawkins, 1971a).

Many of these rias have been choked with sediment since ca. 7000 BP (5000 BC), with much material being deposited off shore, contributing to existing barriers and sand banks. Hails (1975) identifies a number of submerged features in Start Bay, Devon, which include a buried cliff line at a depth of 42m, and a number of relict barriers. He suggests that a barrier-estuarine-lagoon complex has migrated steadily shorewards during the past 8000 years in Start Bay. The presence of these off-shore barrier features is confirmed elsewhere in south west England by Clarke (1969) and Healy (1996a). James (1990) comments that sand banks are a common off-shore feature in coastal sites, and may have obstructed the rising sea-level permitting the development of lagoonal features. There are numerous accounts of a large sand bank at the entrance to the Kingsbridge Estuary (Robinson, 1977; Adey, undated). The presence of a submerged forest is hinted at in a text entitled ‘Kingsbridge and it Surroundings’ (Anonymous, 1874: 169), which describes a wood which is:

‘.... believed to have been overwhelmed by the waves in times remote, and the stumps of a number of large trees, discernible some years ago, strengthen the supposition; some of these may yet be seen at the ebb of spring tides’.

This may be contemporary with a band of peat at 14.70m (-12.90m OD), located during trial boreholes associated with the South West Water installation (Stephen Reed, pers. comm.). Investigation of these deeper sediments is currently the focus of a micropaleontological study to examine sea-level change in this part of south west England (Roland Gehrels, pers. comm.).

4.1.2 Land use and modern vegetation groups

The land use has remained in largely the same state since Anglo-Saxon times. The size of the fields has increased, but they are still used for pasture, although the number of farms growing arable crops has declined. The area of woodland has most likely remained the same since these times, although the woods of Saxon times have been felled, probably to supply the ship building industries of the 18th
and 19th centuries, subsequently replaced by mixed woodlands and plantations, e.g. Collaton Wood and Tor Woods.

The North Sands study site is dominated by wooded valley sides of *Salix* spp., *Quercus* spp., *Aesculus hippocastanum*, *Fagus sylvatica*, and *Alnus glutinosa*, with patches of *Corylus avellana* scrub. *Hedera helix* and *Ilex aquifolium* form a major component of the wooded areas, with *Pteridium aquilinum* prevalent on the more open slopes. Trees extend down to the damp marsh area in the combe bottom. The wetland flora is dominated by *Phragmites australis* with a variety of different *Rumex* and *Carex* species and members of the Poaceae, Cyperaceae and Apiaceae families.

4.2 Sampling regime

Field sampling was carried out by Stephen Reed (Exeter Archaeological Field Unit) using a 7cm diameter piston corer to a depth of 12.50m. Samples were taken in conjunction with the construction of a foul water discharge facility in the immediate area by South West Water Plc. (Plate 4.1).

Laboratory sampling was undertaken following detailed stratigraphical description of the sediment (Troels-Smith, 1955), see section 4.4. Samples were taken at an interval of 30 cm due to the depth of sediment (39 samples in total). Pollen samples were taken at the same levels as those for geochemical analysis. Pollen analysis was undertaken by Mrs. Mary Jack in connection with a pollen analytical study of coastal sediments at the Open University.

4.3 Palaeoenvironmental reconstruction of the North Sands area

Description will initially be made of the stratigraphy of the sediment, followed by a discussion of the geochemical and then pollen analysis results. Multi-variate statistical techniques were used, as presented in section 2.4, to examine the direction of change and grouping of samples with similar geochemical and palynological characteristics through time. This is the first investigation of the EDMA technique using the improved operating and preparation procedures, therefore careful discussion will be made of the efficacy of the technique to produce meaningful palaeoenvironment information.

4.4 Stratigraphical description of the North Sands sediment (Fig 4.3)

The uppermost 1.20m of sediment is missing, as is the material between 1.94 and 2.31m. It was not
Plate 4.1  North Sands viewed from the cliffs above the beach. The plate shows the construction of the South West Water foul water treatment plant. The crane (arrow) marks the approximate location of the sampling site.
2.61 m OD

0
Not retrieved

1

2

3

4

5

6

7

8

9

10

11

12

12.50 m
(-9.89 m OD)

Highly decomposed black peat with monocot. roots, wood fibres and occasional Phragmites rhizones

As above. Some schistose pebbles at 240cm.

Fine, silty peat with no macrofossils.

Compressed woody peat

Black, silty peat

Black, humified silty peat with occasional wood fragments. Schist derived mica fragments evident.

Silty mud/humified peat. Increasing mica fragments with wood remains.

Black silty peat with occasional wood fragments. Mica fragments evident. Fine monocot. fragments from 770cm.

Grey silty peat with shell fragments becoming sandy to base.

Grey silty clay becoming coarser to base.

Coarse gravelly sand in grey silt matrix with occasional organics.

Organic silt/clay with decreasing organic content to silt/clay below.

Grey sand with shell fragments.

Grey silty sand with shell fragments.

Grey silty clay. Occasional shell fragments and organic inclusions. Corylus avellana shell at 1223cm with gnaw marks of Apodemus sylvaticus.

Not retrieved

Highly decomposed black peat. Few recognisable remains.

Silty black peat with very fine sand.

Silty peat with occasional wood fragments.

Wood peat.

Wood peat

Wood

Black, silty humified peat. No mica fragments.

Black silty humified peat with occasional wood fragments. Mica fragments evident. Fine monocot. fragments from 770cm.

Organic silt/clay with decreasing organic content to silt/clay below.

Grey sand with shell fragments.

Grey silty sand with shell fragments.

Grey silty clay. Occasional shell fragments and organic inclusions. Corylus avellana shell at 1223cm with gnaw marks of Apodemus sylvaticus.

Figure 4.3 Stratigraphy of the North Sands sediment
possible to sample these levels due to the semi-liquid state of this material. The sediments immediately overlying bedrock were not recovered in this study due to limitations of the coring equipment used, however, engineers borehole investigations, associated with the installation of the marine discharge, indicate bedrock (grey/green medium grained, narrowly cleaved, highly fractured, slightly weathered schist) occurred at a depth of 16.00m. The engineering test pit was terminated at 16.30m. Immediately above this level (15.25m to 16.00m) the sediments were composed of grey sands with fine to coarse sub-rounded to sub-angular gravels. This in turn was overlain by a peat band between 14.70-15.00m. The next unit was composed of olive green/grey clayey silts, with abundant shell fragments and occasional peat inclusions. Above this unit the sediments are essentially of the same nature of those at the base of the core extracted for this analysis. A calibrated radiocarbon date of 5930-5290 BC was obtained by AMS analysis of a wood fragment taken from a depth of 12.50m (conventional $^{14}$C age: 6705±165 BP, lab code AA-14699).

The basal sediment of the North Sands core is composed primarily of coarse gravels in a silt matrix, with occasional organic inclusions. Above this is a grey silty clay unit with small shell fragments. A nutshell of Corylus avellana was found at 12.23m with gnaw marks of Apodemus sylvaticus (Wood mouse). Overlying this unit the sediment becomes sandier (ca. 11.00m), with frequent shell fragments. The peat/clay interface is a gradual transition encountered at 9.00m. The sediments above this junction are characterised by silty, well humified peat, with alternating micaceous units. A wood layer is encountered at 4.16m, which is in turn overlain by black silty peat, and wood peat. Towards the top of the profile the peat becomes more humified, with few recognisable macrofossil remains. The unit at 2.31m is a highly decomposed peat, but has schistose pebbles at its base. The uppermost unit recovered is a highly decomposed peat with frequent monocotyledonous remains, including rhizomes of Phragmites australis. The top of the core was at a height of 2.61m above OD.

4.5 EDMA geochemical study

For this initial analysis of sediment using EDMA a relatively wide range of elements were analysed i.e. those detailed in section 1.5, in addition to Zn, V and Cl. It was hoped to use these additional elements to: (i) corroborate any indication of sea-level change (Cl) provided by other elements such as Na, K and Ca; (ii) utilise Zn as an additional indicator of anthropogenic activity (Tanskanen, 1976; Stewart and Fergusson, 1994); and finally (iii) investigate Vanadium, which is primarily associated with magmatic rocks in the upper lithosphere (Goldschmidt, 1954), although is present in
a range of different minerals (Day, 1963). This element may therefore be linked to the weathering of these rocks, and the burning of fossil fuels (Hopkins et al., 1977).

The geochemical results are presented as element profiles (Fig. 4.4a,b) divided into six distinct chemizones using the techniques outlined in section 2.4.1, and are described in Table 4.1.

Initial examination of the geochemical data suggest that a number of elements lend very little to the overall interpretation of the site.:

(i) Mn, Cl and Zn all appear to be present in negligible amounts. This is either a problem of detection capabilities of the EDMA technique, or related to the fact that the elements simply were not present in the sediment.

(ii) Cu, V and P suffer from similar problems to those outlined above. All elements display a number of peaks, which are associated with high standard errors, and as such are of questionable utility. This does question the general utility of EDMA for analysis of these types of sediments since V is generally quite abundant with a crustal average of 100ppm (Wedepohl, 1995).

(iii) The heavy metal elements, As, Sn and Pb, exhibit very similar profiles and are probably meaningless due to this.

These points will be addressed through the interpretation and discussion sections of the chapter, but emphasis will be placed upon the more meaningful signals produced by the following elements: Na, K, Ca, Mg, Fe, S, Al and Si.

4.5.1 Multi-variate analysis of geochemical results

The use of these techniques was briefly introduced in 2.4.3. Their application in this study will be used to investigate relationships both between samples and elements through the North Sands sedimentary profile.

DCA of the data produced two plots, the element plot (Fig. 4.5) and the sample plot (Fig. 4.6). The analysis of elements revealed some interesting results. However, only the elements which provide meaningful profiles are presented. It is more informative to examine the position of the elements on the plot with respect to environmental gradients. It seems likely that axis one indicates the
Figure 4.4b
EDMA results from North Sands analysis

Depth (metres below ground surface)

Calendar years
(2 Sigma)
<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (m)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSGa</td>
<td>12.50-11.70</td>
<td>The zone is characterised by rapidly increasing levels of Ca and IC. It displays high levels of Si, Fe, Al and K, although the latter two elements decline steadily to the overlying boundary. The trace elements, Sn, As and Pb all display very similar profiles with small relative amounts.</td>
</tr>
<tr>
<td>NSGb</td>
<td>11.70-8.70</td>
<td>K displays dynamic equilibrium conditions through this zone, with a steadily declining trend. Ca is abundant, reaching peak levels of 18 % at 11.30m, this element declines drastically to the overlying chemizone boundary (&lt;5%). Both Si and Al are abundant and exhibit stable profiles. S is low and fluctuates in this zone, illustrating a zone peak concentration at 9.9m (7%). Low, stable conditions are displayed for Fe, P, Mn, V and Cl. The traces share very similar profile characteristics.</td>
</tr>
<tr>
<td>NSGc</td>
<td>8.70-7.50</td>
<td>The opening of the zone is marked by the reduction of IC and Ca, with TOC increasing to high levels. Si peaks in this zone at 7.8m (55%). S is high but demonstrates dynamic metastable equilibrium conditions at ca. 8m. Al, Ca, K and Mg all display very similar profiles which have low values for the middle three samples of the zone then recover to higher values at the upper chemizone boundary. Cu and Zn display similar profiles, but both display high standard errors for the peaked samples.</td>
</tr>
<tr>
<td>NSGd</td>
<td>7.50-4.22</td>
<td>Fe, K with Si and Al exhibit very similar profiles. All illustrate dynamic metastable equilibrium conditions towards the boundary with NSGe, with a threshold in the upper two samples of the zone. Ca displays steady state equilibrium conditions with an increasing trend to 4.22m. Mg increases gradually through the zone, peaks at 4.8 (7%), before declining through the upper chemizone boundary. P illustrates a peak, with high s.e.'s in the first sample of the zone which declines over the next two samples to low levels of P in the rest of this chemizone.</td>
</tr>
<tr>
<td>NSGe</td>
<td>4.22-2.75</td>
<td>A number of elements display very similar profiles in this zone: Al, Si and K, all of which decline through the lower boundary then increase before declining in the remaining samples. The only elements to increase in this chemizone are the traces and Fe, although the latter decreases in the last sample through the NSGf boundary.</td>
</tr>
<tr>
<td>NSGf</td>
<td>2.75-1.30</td>
<td>S, Fe with TOC characterise this zone exhibiting increased values, while Al, K and Si decline steadily to very low amounts in the uppermost sample. Mg, Na, Ca and Cl all peak in this zone but decline in the top sample.</td>
</tr>
</tbody>
</table>

Table 4.1 Description of North Sands chemizones
Cumulative percentage variance explained by two axes = 59.9%

Figure 4.5 DCA element plot of EDMA data from analysis of North Sands sediment
Figure 4.6 DCA sample plot of EDMA data from analysis of North Sands sediment

Cumulative percentage variance explained by two axes = 59.5%
organic/mineral continuum, with clastic elements generally present on the right of the plot and those elements usually related to organic material on the left. Axis two is a little more ambiguous, but possibly indicates an acidity gradient. The higher base status elements are generally present at the bottom, with those associated with lower pH values occurring towards the top.

The analysis of samples produced a number of groupings, labeled one to four on Fig. 4.6. Group one includes the basal two samples, the second group consists of a number of samples between ca. 9 and 12m. The last two groups include rather mixed samples, but may be divided on the basis of the uppermost samples (group four) and the bulk of the organic sediment samples (group three). The groups relate most clearly to the stratigraphic changes in the sediment, although it must be remembered that the position of samples is determined by the geochemical data, therefore the groups must relate to the element ordination on Fig. 4.5.

A number of questions become apparent after the treatment of these techniques, which will be addressed in subsequent sections of the discussion, and with reference to the results from the pollen analysis:

(i) What is the nature of the marine influence and its associated geochemical signals within the sediment?
(ii) Can the oxidation versus reduction regime of the system be reconstructed?
(iii) What is the nature of the geochemical difference between the organic and the minerogenic sediments?

4.5.2 Interpretation of the geochemical signals from North Sands

The basal sediments: terrestrial versus marine activity

The basal sediment are characterised by alumino-silicate material due to the elevated levels of Al and K. The declining levels of K, with low Na, and increasing values for Ca and IC suggest the increasing influence of marine conditions (Spears, 1973). Si exhibits stable conditions in the basal zone, suggesting a constant input to the system. The form of this Si was confirmed by SEM examination to be quartz sand grains, with no visible input of biogenic siliceous material. However, the input of material with a terrestrial origin is confirmed by the identification of a wood fragment at 12.50m which produced a radiocarbon date of 5930-5290 BC, although it must be stressed that the values for TOC are very low and the incidence of wood fragments in this unit is very occasional in
what must be considered a largely non-organic sediment. This phase relates to group one on Fig. 4.6. The radiocarbon date and the geochemical evidence from these basal sediments agrees well with the assumption made earlier for rising sea-levels in this part of the south west around 7000 BP.

High levels of Ca, IC and shell fragments (Fig. 4.3) in NSGb confirm the presence of carbonate material with a likely marine origin between ca. 9.00 and 11.00m. This evidence suggest the continued influence of marine conditions as the sea continues to rise during the mid-Holocene period. Si and S both exhibit dynamic equilibrium conditions in NSGb, which may relate to the steady increase in biological productivity of the immediate environment; diatoms were located at 9.40 and 11.10m. However, the presence of these two elements may indicate the destabilisation of catchment soils (Shotyk, 1988; Pyatt et al., 1992), and the possible inclusion of wind blown sand from coastal banks (Cowgill and Hutchinson, 1970).

**The cessation of marine influences**

The reduced influence of marine conditions is noted at the boundary between NSGb and NSGc as indicated by the declining values for Ca, K (Spears, 1973) and IC. These samples therefore illustrate the diminishing marine influence with an associated increase in terrestrial processes. The geochemistry of the sediment is dominated by terrestrial processes with an increase of TOC from 8.70m, and the transition from clay to organic silt/clays with an increasing organic content and the development of peat sediments at 8.5m. This transition most likely dates to the attainment of sea-levels similar to today's for this part of the coast, dated in other locations to around 5500 BP (Kidson and Heyworth, 1973; Healy, 1996b).

**The initiation of organic sedimentation**

The rapid rise in organic carbon and the accumulation of black silty peat at 8.50m indicates the first stages of terrestrialisation of the North Sands sedimentary system (NSGc). The geochemical signals of this period are dominated by Si, confirmed to be quartzitic mineral particles following SEM examination of the sediment, most likely wind blown sand from the nearby beach. The peak of P at 7.5m could relate to a nutrient inwash following destabilisation of the surrounding soils, transported as Fe/Mn co-precipitated compounds, since P is noted as having a low solubility under oxidising conditions (Mackereth, 1966). The destabilisation hypothesis is supported by the increased presence of Fe at 7.50m and the increased number of clastic elements at this level: K, Al with slightly lower
levels of organic carbon and S, suggesting disturbance to the accumulating organic system.

*The attainment of geochemical stability*

After ca. 6.75m most of the major elements exhibit dynamic metastable equilibrium, indicating more stable conditions in which the input of chemical compounds to the sediment is constant (NSGd). The increase in organic carbon between 6.75 and 4.80m illustrates the developing status of the organic sediment body. Static profiles for Al, K, Fe and Si corroborate this stability. However, it is suggested that the increasing profiles for Al and Si is linked to the gradual input of alumino-silicate material derived from the local catchment rocks.

*The uppermost sediments*

The presence of a marine inundation phase is possibly suggested by an increase for Ca, Mg and Na around 4.5m. However, no mineral material with a marine origin was deposited on the accumulating mire surface, with Si still linked to the presence of alumino-silicate minerals of a terrestrial origin.

The identification of a wood layer at 4.16m and the diminished base status of the system in NSGe suggests a change in the local conditions. The evidence indicates a modification to the local hydrological and geochemical status of the system, initially creating anaerobic conditions in which sulphides could form. These conditions were short-lived and the system appears to have been systematically acidified as illustrated by the declining amounts of Ca and Mg.

The upper 2.5m of sediment are the most problematic to interpret due to the behaviour of a number of geochemical indicators. The increase for Fe from 1.6m suggests the presence of oxidised conditions, although the accumulation of S at this level may relate to the process of sulphate reduction since Rudd *et al.* (1986) state this to be the major source of S to the sediment. Peaks for Ca and Mg may relate to the erosion of schistose catchment materials following disturbance, and the low presence of other bases would suggest the material introduced to the sediment body was previously subjected to leaching processes, following earlier de-stabilisation phases. However, the continued increase for TOC suggest minimal disturbance to the autogenic processes controlling peat accumulation.
4.6 Pollen analysis of the North Sands sediments

The results are presented as a pollen diagram (Fig. 4.7) and described in Table 4.2. The DCA plots from analysis of the pollen data are presented as a species plot (Fig. 4.8) and a sample plot (Fig. 4.9).

4.6.1 Multi-variate analysis of the North Sands pollen data

The position of taxa on Fig. 4.8 suggest axis one differentiates between relatively undisturbed wood/scrub land and species indicative of more open habitats. It is not clear from the ordination plots the nature of factors differentiated with axis two on Fig. 4.8, or the axes of the sample plot (Fig. 4.9), since no pattern is clearly discernible.

The basal samples fall into a group (I), characterised by the species of group α, indicative of deciduous woodland composed of *Ulmus* and *Hedera* with an epiphytic flora dominated by *Polypodium*. *Pinus* belongs to this group, but would have been present either only very locally, or at some distance from the North Sands site. Group II relates most likely to β on Fig. 4.8, with declining values of dryland arboreal taxa and the increasing dominance of *Alnus*. The next group (III) includes samples between 6.30 and 3.50m and is associated with group χ, a disturbed ecosystem in which damp species become more abundant (*NSP4*) including Cyperaceae and species represented by Pteropsida, with possible indicators of local vegetation disturbance i.e. *Plantago lanceolata*, *Rumex* and Brassicaceae species. The last sample group (V) is associated with the fen communities, *Typha latifolia* and *Sparganium emersum*-type (group ε), although lacks the *Alnus* component of previous zones.

4.6.2 Interpretation of the pollen evidence

The lowermost sample suggests a habitat dominated locally by *Alnus*, although this immediately declines to low values. Indeed it seems likely that this species was present on the sampling site given the high pollen values (ca. 70%). The dryland tree taxa present on the upper slopes at this time were composed of *Quercus*, *Ulmus* and *Corylus avellana*, although *Myrica gale* could equally have formed part of the local wetland flora since these two species are inherently difficult to differentiate palynologically (Godwin, 1975; Edwards, 1981). The local presence of salt marsh is suggested by the identification of pollen grains of the Chenopodiaceae, a large family with distinct affinities for bare ground, often by the sea (Fitter *et al.*, 1985; Rieley and Page, 1990). Additional palynological
Figure 4.7

North Sands Percentage Pollen Diagram

Calendar years (2 sigma) + Indications of trace occurrence (>1% TLPS)
<table>
<thead>
<tr>
<th>LPAZ</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
</table>
| NSP1 | 12.5-11.1  | *Alnus, Corylus, Quercus, Typha latifolia*  
This zone is characterised by high, but fluctuating levels of arboreal pollen dominated by *Alnus*, with smaller components of *Pinus, Ulmus* and *Quercus*. *Corylus* features more consistently, at around 35%. Herbaceous pollen, is sparse and is composed of Poaceae, with smaller amounts of Cyperaceae, Chenopodiaceae and members of the Cardueae/Asteroidae tribe. Spores are well represented and are dominated by *Polypodium*. *Typha latifolia* dominates the wetland taxa. |
| NSP2 | 11.1-9.0   | *Corylus, Alnus, Quercus, Urtica*  
*Alnus* attains peak values in this zone approaching 80% at 10m. *Alnus* appears more consistently at around 20%, with a more diverse herbaceous flora composed of *Urtica, Plantago lanceolata, Filipendula* and *Succisa pratensis*. Spores feature prominently in the zone. |
| NSP3 | 9.0-6.6    | *Alnus, Corylus, Quercus, Typha latifolia*  
Increasing values of *Alnus* and declining *Corylus* characterise this pollen zone. Both *Ulmus* and *Quercus* disappear in the upper levels of the zone. *Hedera* features at the onset of this zone. *Urtica* dominates the herbaceous flora, but disappears to trace levels at 8m. Spores are low, but consistently represented at ca. 10%. *Typha latifolia* marks both the onset and close of NSP3. |
| NSP4 | 6.6-3.5    | *Alnus, Corylus, Cyperaceae, Brassicaceae, Apiaceae, Pteropsida*  
*Alnus* features consistently with an average value of 30%, but displays a significant deviation at 4m (<10%). *Corylus* is low, and stable at ca. 10%, but declines steadily over the zone. Herbaceous pollen is dominated by Cyperaceae, Brassicaceae and Apiaceae, with smaller contributions from Poaceae, *Ranunculus acris* and *Succisa pratensis*. Fluctuating values for *Polypodium* and *Pteridium* contribute to a spore count dominated by undifferentiated monolete spores. |
| NSP5 | 3.5-1.8    | *Alnus, Typha latifolia, Poaceae, Cyperaceae, Brassicaceae, Pteropsida*  
The zone is dominated by high, fluctuating levels of *Pteropsida* and *Alnus*. Herbaceous pollen features significantly in this zone and is characterised by Cyperaceae, Poaceae, Brassicaceae, with smaller components of *Urtica, Rumex, Epilobium*-type, Apiaceae, Lamiaceae and members of the Asteraceae family. *Typha latifolia* reaches peak values in this zone of 40% at 3m. |
| NSP6 | 1.8-1.3    | *Pteropsida, Typha latifolia, Cyperaceae, Brassicaceae, Corylus*  
The spectra of this zone are dominated exclusively by the peak values of undifferentiated monolete spores. Arboreal pollen is sparse with only a trace presence of *Quercus* and *Pinus*. Herbaceous pollen is dominated by Cyperaceae and Brassicaceae, with a small contribution from *Urtica* and Apiaceae in the base of NSP6. |

Table 4.2 Description of North Sands local pollen assemblage zones (LPAZ)

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Figure 4.8  DCA species plot of pollen data from analysis of North Sands sediment (Species shown all have occurrences >1% TLPS in >5 samples).
Cumulative percentage variance explained by two axes = 39.5%

Figure 4.9  DCA sample plot of pollen data from analysis of North Sands sediment
evidence for salt marsh communities is lacking, possibly due to the low pollen production and the largely entomophilous dispersal strategies of these plants. Eutrophic freshwater or brackish conditions are suggested by the appearance of *Typha latifolia* at 12.4m, a species favouring shallow open water, with a pH of greater than 5 (Grime *et al.*, 1988), which may have been growing on the margins of the *Alnus* woodland. However, this species declines rather rapidly through the remaining samples in *NSP1* and is not present in the next pollen zone. This is interpreted as a reduction in freshwater conditions, with an associated increasing marine influence since neither *Typha latifolia* nor *Alnus* will tolerate saline conditions. By 12.00m the local *Alnus* dominated woodland has retracted considerably, most likely up the combe away from the sampling site and the advancing sea. This effectively allows a greater proportion of the extra-local pollen component (Jacobson and Bradshaw, 1981) on to the surface of the accumulating sediment. The surrounding environment at this time is dominated by *Corylus avellana* on the drier slopes, with a consistent fern component probably present in an understory-type habitat.

The next stage of development (10.00m) is marked by a sharp reduction of *Corylus* pollen which seems likely to be the result of either a diminished flowering efficiency or deforestation of this species. It is possible that management of *Corylus* may have been occurring since the species may be considered a valuable resource (Zvelebil, 1994).

The opening of *NSP3* reveals an increase in *Alnus* pollen values and a reappearance of *Typha latifolia*, again suggesting less saline conditions in the immediate locality. The sustained presence of *Alnus* which increases through *NSP3* suggests a re-advancement and closing of this damp woodland habitat on to the sampling site. Again it seems possible that the dense woodland could have effectively filtered extra-local and regional pollen components (Tauber, 1965). This would explain the diminished amount of *Corylus avellana* pollen reaching the sampling site. However, increased indications for disturbance in the environment are found in the next pollen zone (*NSP4*). Low levels of *Corylus* in association with an increased herbaceous flora, composed of sedges, grasses, and members of the Apiaceae family, which include species such as *Crithmum maritimum*, *Oenanthe lachenalii*, *Apium graveolens* and *Peucedanum officinale*, suggests a more open environment. The species mentioned are all frequently encountered in wet places and marshes, particularly by the sea (Stace, 1991). This zone also contains members of the Brassicaceae family, a large group of plants which are present in a number of different habitat types, including coastal areas e.g. *Crambe*
maritima, Matthiola incana, M. sinuata and Cochlearia anglica.

The opening of NSP5 is marked by the reappearance of Typha latifolia suggesting a reversion to the damper eutrophic conditions experienced in the basal zone. It is accompanied by an expansion of Cyperaceae pollen and a significant increase of fern spores. This evidence indicates a reversion to swamp conditions on the sampling site, in a local habitat characterised by a more open species rich herbaceous flora with a declining Alnus woodland cover similar to the present day situation at North Sands.

4.7 Discussion of the palaeoenvironmental development of the North Sands area

The basal sediments from North Sands have accumulated under eutrophic conditions characterised by local Alnus fen woodland with Typha latifolia forming a sub-dominant component of the flora (Fig. 4.10, Table 4.3). This hypothesis is corroborated with reference to the geochemical evidence, which displays elevated levels of K. However, this environment seems short-lived and is replaced by conditions indicating increased marine activity, in which K and Al decline and are replaced by high levels of Ca, IC with much shell material. Alnus pollen declines sharply, most probably in response to the rising sea-level. This suggests a movement of the fen woodland northwards away from the sampling location. Further evidence for elevated sea-levels is provided by the decline of Typha latifolia at 11.00m. The persistence of high amounts of Si through NSGb is most likely due to wind-blown material from the beach. Continued marine influence is interpreted from the sediments between 9.00 and 11.00m due to the sustained levels of Ca, IC and the identification of shell fragments throughout this stratigraphic unit. The pollen spectra of NSP2 is dominated largely by dryland arboreal taxa suggesting the relatively open nature of the accumulating sediment system at this time.

It has been suggested in other parts of the coast that a number of sedimentary systems have developed immediately behind morpho-sedimentary structures (Healy, 1995, 1996a,b; French, 1996) which developed during the mid-Holocene. This was a time of significant sea-level change (Hawkins, 1971a; Kidson and Heyworth, 1973; Heyworth and Kidson, 1982) and much movement of sediment rich features in this part of the south Devon coast (Clarke, 1969; Hails, 1975). It is likely that the transition from marine to terrestrial sedimentation, which occurs around 9.00m, is due to such a feature moving onshore with the rising sea-level which effectively cut off the lower reaches.
<table>
<thead>
<tr>
<th>Time</th>
<th>Geochemistry</th>
<th>Vegetation</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>Fe with Ca and Mg, much TOC</td>
<td>Sparse AP. Cyperaceae and Brassicaceae dominate spectra</td>
<td>Damp eutrophic conditions</td>
</tr>
<tr>
<td>3500 BC</td>
<td>Increased Ca, Mg, Na</td>
<td><em>Alnus</em>, much NAP</td>
<td>Possible deforestation linked erosion episode</td>
</tr>
<tr>
<td></td>
<td>Stable Al, K, Fe, Si</td>
<td><em>Alnus</em>, much NAP</td>
<td>Deforestation. Lower <em>Alnus</em> and <em>Corylus</em></td>
</tr>
<tr>
<td></td>
<td>Increase Fe, K, Al, lower TOC and S</td>
<td>Increasing <em>Alnus</em>, declining <em>Corylus</em>, <em>Typha latifolia</em></td>
<td>Closed damp woodland conditions</td>
</tr>
<tr>
<td></td>
<td>Declining Ca, K, increasing TOC</td>
<td><em>Corylus avellana</em>, <em>Alnus</em> increasing NAP</td>
<td>Cessation of marine conditions. Organic sedimentation initiates, <em>Alnus</em> moves back onto site</td>
</tr>
<tr>
<td>5000 BC</td>
<td>Increasing Ca, IC, much Si</td>
<td><em>Alnus</em>, mixed dryland arboreal species. <em>Typha latifolia</em></td>
<td>Increasing marine influence, movement of <em>Alnus</em> up combe</td>
</tr>
</tbody>
</table>

Table 4.3 Summary of the palaeoenvironmental development of North Sands, south Devon.
1 Initial state of system

Alnus fen dominates local environment, with a marginal component of Typha latifolia. Geochemical indicators suggest an increasing marine influence (Ca and IC).

2 Terrestrial versus marine conditions

Increasing levels of Ca and IC between 9.00 and 11.00m suggest the presence of marine conditions. The palynological evidence indicates a movement of Alnus away from the sampling site, resulting in a more open environment in which regional pollen is detected. The presence of a sand bank at the mouth of North Sands bay is suggested to move on shore with the rising sea-level of this mid-Holocene period.

3 Stability

The geochemical evidence suggests stable conditions (Fe, Si, Al and K) under which autogenic processes result in the steady accumulation of organic sediment. The pollen data suggest a readvancement of Alnus on to the site. The extent of both the dryland and damp woodland declines and is replaced by an increased herbaceous component to the flora.

4 The current situation

The environment at North Sands is presently characterised by open conditions with pockets of deciduous woodland. The character of vegetation has been described previously (4.1.2). The geochemical data associated with this period seem to indicate signals largely linked to acrotelm processes (Fe and S).

Figure 4.10 Schematic development of North Sands sedimentary system (Progression 1 through 4).
of the combe to marine influences. The event results in a reduction in the indicators of marine conditions, Ca, IC and the shell fragments, and an increase in TOC. A date of ca. 3500 BC (5500 BP) may be suggested for this incident due to similar events along the coast of south west England (Kidson and Heyworth, 1973; Healy, 1995). The steady decline of a number of elements for this phase of activity is interpreted as a gradual advancement of the sand bar and subsequent closing of the lower reach of the combe to marine influences (Fig. 4.10).

The next stage of development is characterised by a development of *Alnus* woodland in the immediate vicinity of the sampling site. This effectively filters out most of the extra-local pollen as the woodland closes. The stability of the system during this phase is reflected by the static nature of a number of elements, and the continued accumulation of TOC in NSGd. The palynological data suggest more open conditions with a decrease in both the extent of *Corylus avellana* and *Alnus* with a subsequent expansion of herbaceous taxa indicative of open, damp, disturbed habitats.

The wood layer at 4.16m resembled that of *Alnus* although poor preservation made it difficult to make a definite identification, again corroborating the fact that fen woodland existed in the immediate locality of the sampling site. The geochemical conditions associated with this wood layer indicate locally anaerobic conditions in which sulphides could form, however this stage appears to be rather short lived.

The uppermost sediments suggest a return to damp eutrophic conditions on the sampling site given the high values for *Typha latifolia* (ca. 40% at 3.1m), with an increased presence of sedges (Fig. 4.7). The geochemical signals associated with this phase are rather difficult to interpret in terms of palaeoenvironmental processes and most likely relate to modern acrotelm processes.

4.8 Discussion

The results from EDMA and pollen analysis of the sediments from North Sands were generally complementary. Both techniques indicated the presence of eutrophic conditions in the basal samples as illustrated by group one on Fig. 4.6. The geochemical data illustrates the nature of the marine sediments between 9.00 and 11.00m (Group two, Fig. 4.6). The return to eutrophic freshwater conditions at 9.00m is shown by the decrease of Ca and IC, increasing TOC with S and the identification of *Typha latifolia* pollen. The stability phase illustrated by the geochemistry relates to
the development of *Alnus* woodland on the site (Group three, Fig. 4.6).

With respect to the questions posed at the outset regarding the utility of the geochemical signals to provide information on a number of different environmental activities and processes, it seemed likely that the geochemistry of Si and Al were linked strongly to the presence of alumino-silicate minerals, particularly after 9.00m. Fe seemed to be of some use in determining the redox regime of the system particularly in the upper levels of the profile, with S seemingly relating to the production of sulphides in the anaerobic zone experienced around 4.2m, associated with the closed *Alnus* woodland at this time. Ca proved useful in the examination of the marine activity, especially in the lower 3.5m of the profile, its activity in the organic sediments apparently linked to the presence of clastic material from the surrounding catchment slopes, as does K and to some extent Mg.

However, a number of elements produced no meaningful data in this analysis: the heavy metal elements, together with P, V, Cl, and Zn. The problem with these elements remains to be investigated in the other sites, but Zn, Cl and V will be excluded from further analysis due to the limited potential use of these elements in the other upland sites. The problem with this suite of elements may be of an analytical nature, associated with the detection capabilities of the EDMA technique.

4.9 Conclusions

EDMA of the North Sands sediment produced significant information about the nature of the palaeoenvironments in this area of the Kingsbridge Estuary. The focus of study will now move to the investigation of a number of sites on the Dartmoor upland, and will address a range of different research questions, using material from different types of sedimentary environment to fully investigate the usefulness of the EDMA technique.
Chapter 5

Palaeoenvironmental investigations at Tor Royal, central Dartmoor

5.0 Introduction

This chapter presents the results from analyses conducted at the highest of the Dartmoor sites (Fig 5.1). It will follow on from the work undertaken at North Sands further testing the utility of EDMA in a very different environmental and sedimentary context.

Tor Royal provides a significant opportunity to explore anthropogenic activity from late Mesolithic times on Dartmoor. Analysis is of particular significance since post-Iron Age records of environmental change are under represented in palaeoenvironmental data collected from Dartmoor since the early work of Simmons (1962, 1964a,b). The bulk of the existing pollen diagrams from the upland are also hampered by a number of problems including destruction/truncation by draining, peat cutting and mineral extraction processes (Caseldine and Maguire, 1986).

The ombrotrophic nature of the upper sediments provides an excellent opportunity to examine the regional patterns of change occurring in the central Dartmoor area, both in terms of the vegetation change and the flux of heavy metals and mineral material transported aerially and deposited directly on to the site.

5.1 Site location, morphology and age

Tor Royal (SX 602728) lies approximately 1.3km south east of Princetown at a height of ca. 390m (Fig. 5.1). The vegetation is typical of an ombrotrophic mire, with ericaceous shrubs, Tricophorum cespitosus, Eriophorum spp. and Sphagnum mosses. An unusual feature of the vegetation is the abundant Rhynchospora alba. The surface and subsurface morphology of the bog was constructed by probing in two separate transects across the surface, each levelled to OD (Fig. 5.2). This revealed the bog to consist of a single sediment body lying in a smooth valley trending north-south (Plate 5.1). The surface of the bog is domed, with the apex of the dome offset to the north east. It is therefore an eccentric raised mire (Heathwaite et al., 1993). The southern area of the bog appears to lobe and end quite abruptly, with a more gradual thinning of peat experienced to the northern edge. A number of drainage channels have been cut across the surface, all of which seem to drain westwards in to a larger channel. The origin of the ditches and channel is unknown at present, but it is suspected they
Figure 5.1 Location of Tor Royal mire
Broken lines indicate the extrapolated sub-surface morphology, with solid lines indicating ground surface.

Figure 5.2  Morphology of the Tor Royal ombrotrophic mire
Figure 5.3  Age-depth profile of the Tor Royal sediment. Vertical bars represent depth of sediment submitted for dating, horizontal bars indicate calibrated calendar ages.
were used to aid peat cutting operations as a number of cutters hollows can be found around the margins of the site (Plate 5.2). However, there are no signs of physical disturbance beyond the extreme margins of the western portion of the mire and the pollen and stratigraphical records do not contain noticeable hiatuses.

Radiocarbon dating suggests the system to have initiated around 5000 BC and to have accumulated at an average rate of ca. 0.09 cm yr⁻¹ (Table 5.1). This site therefore has the potential to provide a high temporal resolution palaeoenvironmental history for central Dartmoor.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Lab-code</th>
<th>(^{14}C) age</th>
<th>Calibrated age (BP)</th>
<th>Calendar age (ref AD 1950)</th>
<th>Accumulation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-100</td>
<td>SRR-5715</td>
<td>840±45</td>
<td>900-670</td>
<td>AD 1050-1285</td>
<td>0.124</td>
</tr>
<tr>
<td>150-170</td>
<td>SRR-5716</td>
<td>1460±45</td>
<td>1410-1290</td>
<td>AD 540-660</td>
<td>0.09</td>
</tr>
<tr>
<td>230-250</td>
<td>SRR-5717</td>
<td>2240±45</td>
<td>2345-2130</td>
<td>395-180 BC</td>
<td>0.074</td>
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<tr>
<td>366-380</td>
<td>Beta-93822</td>
<td>3700±90</td>
<td>4340-3730</td>
<td>2390-1780 BC</td>
<td>0.082</td>
</tr>
<tr>
<td>471-485</td>
<td>Beta-93823</td>
<td>4650±90</td>
<td>5590-5050</td>
<td>3640-3100 BC</td>
<td>0.075</td>
</tr>
<tr>
<td>574-859</td>
<td>Beta-93824</td>
<td>5890±70</td>
<td>6880-6530</td>
<td>4930-4580 BC</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Radiocarbon dating results for Tor Royal

5.2 Sampling regime

Samples were collected from the deepest point of the mire (6.23m). Six samples were taken for radiocarbon dating from the profile (Table 5.1, Fig. 5.3). Each monolith was described in the field using Troels-Smith (1955) classification, and subsequently re-examined in the laboratory to confirm initial identifications (Fig. 5.4). A total of 48 samples were prepared for EDMA, pollen, Total Organic Carbon (TOC) analyses and ashing at 900°C to give an indication of the mineral content of the sediment (Aaby, 1986). Samples were taken at 5cm intervals for the top 35cm, with the aim of detecting the exotic pollen of the coniferous plantations located around the fringes to the site (Plate 5.2), at Beardown Hill (ca. 3.5km to the north) and from the extensive tracts of woodland around Burrator Reservoir (ca. 5km to the south west). Documentary evidence suggests these plantations are no older than 200 years (Simmons, 1962; Staines, 1974). The remaining samples were taken at 15cm intervals throughout the profile.
Plate 5.1  Tor Royal ombrotrophic mire, central Dartmoor (view east).

Plate 5.2  The margins of the mire looking west towards relict peat cutters hollows (*), with coniferous plantations located in the background.
Figure 5.4 Stratigraphy of the Tor Royal sediment

390.46mAOD

- **AD 1050-1285**
  - Very fibrous, felted peat. Abundant modern roots and macros.  
  - nig. 2 strf.0 elas.3 sicc.1 humo.0 Th2 Dg2

- **AD 540-660**
  - Very fibrous peat, frequent monocotyledonous fragments.  
  - nig.2 strf.0 elas.3 sicc.1 humo.0 Tb3 Dg1

- **395-180 BC**
  - Fibrous peat with fragments of Eriophorum evident.  
  - nig.2 strf.1 elas.3 sicc.1 humo.0 Th3(Eriophonim) Dg1

- **2390-1780 BC**
  - Fibrous peat, much root material, becoming more humified with depth.  
  - nig.2 strf.1 elas.3 sicc.2 humo.1 Th2 Ti1 Dg1

- **3640-3100 BC**
  - Fibrous unit, much root material with abundant monocotyledonous fragments.  
  - nig.2 strf.0 elas.3 sicc.1 humo.0 Tb3 Dg1

- **4930-4580 BC**
  - Well humified compact peat with few macro remains.  
  - nig.4 strf.1 elas.1 sicc.3/4 humo.4 Sh4 Dl+(lignum)
5.3 Palaeoenvironmental reconstruction of the Tor Royal sediment

Discussion will initially be made of the stratigraphy of the sediment followed by a reflection of the geochemical and pollen results. Multi-variate techniques were used, as presented in 2.4, and are shown to be of some use in the interpretation of geochemical and palynological signals from the previous site (see 4.5.1 and 4.6.1).

5.3.1 Stratigraphical description

The basal sediments are characterised by a well humified compact peat containing few wood fragments (Fig. 5.4). This sediment developed somewhere around 5000 BC. The stratigraphy varies very little through the profile, and is composed generally of felted/fibrous material differing only in respect to the degree of humification. The unit between 290 and 313cm exhibits an increase in fine root material with the over lying units displaying much better preserved macrofossil remains. Fragments of Eriophorum are evident in the unit above 170cm, with an increasing frequency of monocotyledonous material. The upper unit (0-10cm) is characterised by modern roots and Cyperaceae fragments. The division between minerotrophic and ombrotrophic status is not apparent from the stratigraphy of the profile.

5.3.2 EDMA investigation

Geochemical investigation of the sediment offered the opportunity to examine the potential of the sediment body to reveal patterns of atmospheric deposition of materials once the system had gained ombrotrophic status, as well as the autogenic signals associated with the accumulation and development of this type of system. EDMA results are presented as element profiles (Fig. 5.5a,b) divided into six distinct chemizones (Table 5.2).

Initial indications suggest the profiles of P, K, Mn, Sn, As and Pb (except for the upper samples) to be of limited use for the investigation of palaeoenvironmental processes from Tor Royal, since these elements either display inter-correlated profile features (heavy metals and Mn) or profiles with isolated peaks which are associated with wide standard error bars (P and K). Discussion will therefore focus upon the information provided by the major elements, Si, Al, the mobile elements, Fe, S and the bases Na, Ca and Mg.
5.3.3 Multi-variate analysis of the Tor Royal EDMA data

DCA of the Tor Royal geochemical data produced an element plot (Fig. 5.6) and a sample plot (Fig. 5.7). Axis two on Fig 5.6 seems to relate to the balance between mineral matter and organic material, with the former including an association between elements such as Al, K, Si and %ash, and the latter displaying a relationship between TOC, S and Ca. Axis one is more difficult to explain but may represent the pH regime of the system through time with elements associated with high base conditions located to the right of the plot.

Analysis of the samples produced a somewhat circular pattern in which the samples from the basal zone and the upper most samples share geochemical signals (Fig. 5.7). Group two includes samples between 500 and 575cm, and as such relates to the phases of declining Fe and lower levels of mineral material. Group three seems to continue the trend of the previous group in which a number of elements attain low, stable profiles (TRGc). The division between groups three and four identifies a major change in the elemental profiles from Tor Royal, the final disappearance of Fe, possibly indicating the position of the minerotrophic/ombrotrophic boundary. Group five identifies the uppermost group of samples which display highly fluctuating profiles, possibly as a result of modern acrotelm processes.

The primary use of the DCA technique is to aid evaluation of the different stages in the development of this peatland system, particularly focusing on:

(i) The initial status of the system, and how it differs from the overlying sediments.
(ii) The nature of the minerotrophic/ombrotrophic boundary.
(iii) Whether the upper sediments contain a greater proportion of anthropogenic signals.

5.3.4 Interpretation of the geochemical signals from Tor Royal

Analysis of the sediment has made it possible to interpret the signals in terms of a number of specific processes operational both within the developing peatland and externally in the surrounding catchment. These will be addressed in the following sections. It is noteworthy to comment on the ash curve at this point. The ash contents of the peats exhibit a 'C' shaped profile which is characteristic of bog profiles (Sillanpää, 1972) due to the incorporation of basal mineral material as the bog plants become established, and the more recent contribution of airborne dust particles. At the top and bottom ash values approach 10%, between 50 and 550cm however, the ash contents are generally
Figure 5.5b  EDMA results from Tor Royal sediment
<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRGa</td>
<td>622-605</td>
<td>This zone is characterised by high, but falling levels of Si and Al, which seem to relate to the high levels of mineral material in the basal samples (ca. 6% at 622cm). Na is suggested to be linked to this material and shows a similar profile. Fe, S and TOC increase in this zone, while the trace elements, Sn, As, Cu and Pb display little variation.</td>
</tr>
<tr>
<td>TRGb</td>
<td>605-462</td>
<td>Dynamic equilibrium conditions are exhibited by Fe in this zone which falls from 35% at 560cm to &lt;20% at 462cm. Al, Si and the mineral fraction continue to decline, all attaining very low values by 560cm. S continues to increase through this zone, with TOC displaying stable equilibrium conditions. P, K, Ca display trace occurrences, while the trace elements display intercorrelated profiles. Mg increases towards the boundary with the overlying zone.</td>
</tr>
<tr>
<td>TRGc</td>
<td>462-357</td>
<td>This zone is marked by the decline of Fe, which disappears at 357cm. Mg peaks at 440cm reaching ca. 8%. The continued increase of S is noted, but dynamic equilibrium conditions exhibiting a declining trend are displayed for TOC. The trace elements, As, Sn and Pb, display interrelation, with Cu fluctuating somewhat stochastically. P, K and Ca are consistently low.</td>
</tr>
<tr>
<td>TRGd</td>
<td>357-72</td>
<td>The significant feature of this zone is the increase in Ca which is sustained throughout the chemizone. Mg, Cu, S and Si display stable equilibrium conditions, while Al peaks at 290cm (ca. 10%), and Na displays elevated values between 140 and 300cm (1-4%). TOC continues to display declining dynamic equilibrium conditions. P and K display random peaks.</td>
</tr>
<tr>
<td>TRGe</td>
<td>72-22</td>
<td>Si, Al, Na and mineral matter display an increased presence in this zone. Mg, Ca decline over the same profile depths. Peaks for Fe and K mark the onset of the zone. TOC and S both decline over this zone. The trace elements, As, Pb and Sn display very similar profile characteristics.</td>
</tr>
<tr>
<td>TRGf</td>
<td>22-0</td>
<td>In this zone many of the elements display stochastic behaviour, probably due to acrotelm processes. The levels of mineral matter continue to increase which corresponds to a sharp decline in the values for TOC.</td>
</tr>
</tbody>
</table>

Table 5.2 EDMA results from analysis of Tor Royal sediment

131
Cumulative percentage variance explained by two axes = 55.7%

Figure 5.6  DCA element plot of EDMA data from analysis of Tor Royal sediment
Cumulative percentage variance explained by two axes = 55.7%

Figure 5.7  DCA sample plot of EDMA data from analysis of Tor Royal sediment

133
around 2%. The relatively low concentrations of ash confirm the ombrotrophic nature of the upper peats, and indicate that metals and mineral materials in the peats were supplied primarily by atmospheric deposition.

Soil erosion and catchment stability

The erosion of stable clastic material into a sediment would typically be indicated by a clear relationship between K, Al, Si, Ca and Mg present in high concentrations (Mackereth, 1965, 1966; Pennington et al., 1972; Gill, 1989; Pyatt et al., 1995). This combination of elements does not occur anywhere in the profile, but it seems likely that the levels of Si, Al and %ash in the basal and uppermost sediments relate to the inclusion of alumino-silicate material from the local rocks and exposed soils. However, care must be taken when interpreting ashed peat values in terms of the proportion of mineral matter, particularly in the upper sediments since bio-elements (Ca, Mg, Si etc.) may contribute significantly to the ash fraction, thus inflating the actual mineral content of the peat (Bill Shotyk, pers. comm.). Si is frequently derived in large proportions from erosion of exposed soils (Goldschmidt, 1954; Shotyk, 1988; Pyatt et al., 1992). Cowgill and Hutchinson (1970) state that Si frequently occurs in association with alumino-silicate minerals, here probably derived from decaying granite. The incorporation of basal mineral material is also reflected in the low carbon content at these depths. Raised levels of Ca, Al and Si above 306cm (TRGd) correspond to the period of continued landscape disturbance reflected by the pollen (section 5.4.7), and relate to increased inclusion of locally derived wind blown material. Further sources of such materials in the upper part of the profile could result from quarrying (e.g. Merrivale), china clay extraction (Lee Moor), and local infrastructure developments such as the installation of a number of railways in the early 19th century. The decreasing carbon content lends support to this disturbance hypothesis.

Acidity changes in the mire and catchment soils

The low presence of base elements in the core suggest the basin and its sediments were acidic from ca. 4500 BC, since these elements have a low affinity for humic substances and are readily lost from peatland ecosystems (Damman 1978; Shotyk, 1988). The acidity of the sediment early in the Holocene is further corroborated by the absence of Mg in the lower sections of the profile. The progressive increase with depth for this element may be a function of diagenesis (Damman, 1978), and with the exception of the basal part of the profile, the palaeoenvironmental use of the element has been lost. A number of possibilities exist to explain the elevated levels of Fe in the basal section
of the core. Firstly, the signal may indicate the fossil Fe signature of the sediment. The declining profile between 450 and 550cm would therefore serve to indicate the increasingly anaerobic sedimentary environment. However, since it seems that the sediment was becoming acidic and anaerobic as suggested by the absence of base elements, increased formation of sulphides and the changing nature of the flora at this time, any Fe present then would have most likely been mobilised and lost from the system in the drainage waters since it is generally mobilised under anaerobic conditions (Goldschmidt, 1954; Mackereth, 1966; Naucke et al., 1993). A second possibility relates to the modern drainage of soil water from the western side of Royal Hill (Fig. 5.1). This water would move down hill as groundwater throughflow and into the margins of the peat mass where it then moves laterally through the sediment. The presence of this element may therefore relate to the influence of modern groundwater in the basal sections of the peat body, which agrees well with the results of a number of other workers (Chapman, 1964; Green and Pearson, 1977; Mannion, 1979). This effect is only limited to the basal two metres of sediment, with the upper four metres supplied solely by atmospheric precipitation. The third possibility includes the mobilisation of Fe from the upper levels following anaerobic surficial conditions (possibly seasonal waterlogging), to deeper levels where the element is sedimented with particulate organic matter. It seems highly likely that the last two hypotheses are the most likely in this environment and thus suggest the limited utility of this element in providing palaeoenvironmental information.

Industrial activity

A potentially useful application of EDMA is to detect periods of industrial activity, in this locality dominated by tinworking and the post extraction stamping and smelting processes. It would also be expected that evidence of the Industrial Revolution would be recovered and could be used as an additional source of dating. The profiles for Sn, As and Pb all have similar patterns throughout the profile. This may record anthropogenic exploitation of metal resources on Dartmoor, but may be a function of the expression of the data as percentages. As the amounts of these elements are low by comparison with other elements, they may be strongly affected by changes in the total elemental composition, reducing the use of these elements significantly. A further problem may be due to the detection capabilities of the EDMA technique, especially given the low concentrations of these elements in this type of system. This will be discussed with respect to the results obtained from analysis of other sites, and with comparison to other analytical techniques in Chapter 9.
The interpretation of the Cu profile is less problematic. Cu is one of the elements that is generally considered to be immobile under anaerobic conditions, due most likely to a combination of sulphate reduction and the formation of metal and organic complexes (Livett et al., 1979; Hermann and Neumann-Mahlkau, 1985; Shotyk, 1988; Stewart and Fergusson, 1994). It does not display the inter-correlation of the other trace metals and displays relatively high values (up to 30%). Therefore, it seems possible that the Cu profile relates to the conditions of accumulation at any given position. However, there is no suggestion of raised values at the depths where anthropogenic inputs of the metal would be likely, during the Industrial Revolution and modern times (Hong et al., 1996). Increased values are present before 2000 BC, a time for which anthropogenic inputs are very unlikely. This suggests the profile may result either from post depositional diagenetic effects or is dominated by autogenic processes, with minimal external influences.

*Mire development processes*

Natural soils exhibit a net gain of organic substances of generally acid character (e.g. humus), which can form compounds with Fe and other metals (Goldschmidt, 1954). The C profile from Tor Royal increases from 623 to 560cm (4400-5500 BC), which is indicative of the developing peat system with organic material contributing the bulk of TOC. However, from this point up through the profile it exhibits a gradual decrease, which perhaps suggests the increasing influence of wind and precipitation borne mineral matter. Brown (1985) states that 90% of the total S in valley mire peats is associated with organic matter. Thus, the S signal obtained from the bog is dominated by processes operational within the sediment body. The increase in S through the profile to 80cm (AD 1200) relates to the development of the peat system, and the accumulation of sulphide rich organic matter through time. Declining values in the upper sediments are associated with aerobic conditions in the acrotelm. Acrotelm activity also affects Fe, and elevated levels in the upper most sediments are a result of precipitation under aerobic conditions. Fluctuating P values may also be linked to aerobic activity, although levels are very low and probably below reliable detection limits (see below). The geochemistry suggests the acrotelm-catotelm boundary is at 15-20cm depth (*TRGf*). This is consistent with measured water table depths on the site (Woodland, 1996).

*Other elements*

There are a group of elements which do not fluctuate throughout the profile in any meaningful way and do not appear to yield useful palaeoenvironmental information. P and K remain at extremely low
values apart from in the acrotelm. K has probably been leached from the peat since it will have been present in a mobile form (Ahti, 1984). While P is often used as an indicator of past anthropogenic activity in soil from archaeological contexts, the Tor Royal record does not reflect such activity. Phosphorus is a difficult element to interpret since there are many different processes which control its availability. The sedimentation of P may be initiated by a number of factors: (i) carried into solution with Fe and Mn under anaerobis; and (ii) precipitated into organic material. The first being important both to the precipitation, as well as the retention of the element in the sediment body (Mackereth, 1966). Shotyk (1988) states the geochemistry of P in mire waters is most likely related to the concentration of dissolved organic C, Fe and the pH, with the capacity of peat to uptake P essentially being a function of mineral content (Naucke et al., 1993). Sedimentation of autogenic P may be through the biological uptake of dissolved inorganic P, with subsequent deposition as particulate organic P (Engstrom and Wright, 1984). It seems possible that the higher levels of P in the basal section of the profile may relate to the inclusion of the element from basal mineral material, although the wide errors bars for the element reduce the confidence of this suggestion.

Although Mn has a similar geochemistry to Fe, low levels throughout the profile are probably due to enhanced mobility under anaerobic conditions, resulting in post-depositional leaching.

5.4.5 Pollen analysis of the Tor Royal sediment

Palynological investigation of Tor Royal has the potential to provide a significant contribution to the general understanding of the vegetation history of central Dartmoor for the period extending from late Neolithic to modern times, with high resolution information available for the latter phases of the archaeological period which are generally poorly covered by existing pollen profiles.

The results are presented as a pollen diagram (Fig. 5.8) and described in Table 5.3. The data are shown as percentages of Total Land Pollen and Spores (TLPS) minus Sphagnum. The DCA plots from the data analysis are presented as follows: the species plot (Fig. 5.9) and the sample plot (Fig. 5.10).

5.4.6 Multi-variate analysis of the Tor Royal pollen data

DCA plots of the pollen data reveal three groups: $\alpha$, $\beta$ and $\chi$. The first relates to woodland conditions in the basal levels of the profile and is composed of Pinus, Betula, Ulmus, Quercus and
Figure 5.8

Tor Royal percentage pollen diagram
Exaggeration factor x10, + indicates a trace occurrence (<1% TLP)

Calendar years (2 sigma)

<table>
<thead>
<tr>
<th>Depth in cms</th>
<th>450</th>
<th>350</th>
<th>250</th>
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<td></td>
</tr>
</tbody>
</table>

Poaceae
Poaceae >40 microns
Cyperaceae undiff.
Plantaginaceae undiff.
Plantago lanceolata
P. major/media undiff.
Ranunculus acris-type
Brassicaceae
Urtica dioica
Cyperaceae undiff.
Caryophyllaceae
Polygnum
Rumex undiff.
R. acetosella
R. acetosa
Hypericum perforatum-type
Drosera intermedia
Lysimachia vulgaris-type
Anagallis tenella-type
Saxifraga stellaris-type
S. hirsuta-type
S. oppositifolia-type
Rosaceae undiff.
Filipendula
Potentilla-type
Lotus
Polygala
Apiaceae
Solanum dulcamara
Lamiaceae undiff.
Melampyrum
Rubiaceae
Succisa pratensis
Scabiosa columbiana
Cardueae/Asteroidae undiff.
Cirsium-type
Lactucae undiff.
Solidago virgaurea-type
Artemisia-type
Achillea-type

Analys: Steve Weas, 1995
<table>
<thead>
<tr>
<th>LPAZ</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
</table>
| TR1  | 622-580    | *Corylus, Betula, Quercus, Ulmus, Poaceae, Potentilla*  
The zone is dominated by *Corylus*, which declines steadily from 45% at 623cm to 30% at the upper zone boundary. Arboreal pollen is well represented. *Betula* declines sharply in this zone. Poaceae increases dramatically, with a wide range of herbaceous species present. The ferns, *Pteridium* and *Polypodium* are present. Significant amounts of charcoal are present in this zone. |
| TR2  | 580-477    | *Corylus, Quercus, Ulmus, Alnus, Calluna, Poaceae, Cyperaceae*  
*Corylus* continues to dominate the spectra, with an increasing *Quercus* component. *Alnus* appears for the first time, attaining a stable profile of ca. 10%. *Calluna vulgaris* increases significantly, whilst Poaceae remains a significant element of the spectra. Cyperaceae features consistently, increasing only in the upper sample of the LPAZ. A lower diversity of herbaceous taxa is noted in this zone. The boundary between TR2 and TR3 is marked by a dramatic peak in *Sphagnum*. High levels of charcoal are present. |
| TR3  | 477-373    | *Corylus, Quercus, Alnus, Calluna, Cyperaceae*  
Cyperaceae rises to high levels peaking with 55% TLP at 390cm. The arboreal taxa fluctuate very little. *Calluna vulgaris* declines through the zone. Poaceae is present in low amounts (5%). High levels of charcoal are found towards the upper LPAZ boundary. |
| TR4  | 373-237    | *Corylus, Alnus, Quercus, Calluna, Poaceae, Cyperaceae, Plantago lanceolata, Pteridium aquilinum*  
*Corylus* dominates the spectra. *Fagus sylvatica* and *Sorbus* appear for the first time. *Calluna* fluctuates widely, peaking at ca. 320cm. *P. lanceolata* first appears and is associated with an expanding herbaceous component. Poaceae increases marginally, while Cyperaceae declines before increasing through the upper boundary. Cereal type pollen grains are first identified at 280cm. *Pteridium aquilinum* is consistent. Stable levels of charcoal are experienced. |
| TR5  | 237-132    | *Corylus, Alnus, Quercus, Calluna, Poaceae, Cyperaceae, P. lanceolata*  
*Corylus* declines, with the arboreal taxa remaining consistently represented in low amounts. *Calluna* remains a significant component of the spectra, although the increased presence of Poaceae and Cyperaceae is noted. *P. lanceolata*, *Rumex acetosa*, *Potentilla* and members of the Asteraceae all attain levels >1% in this zone. Cereal type pollen grains are present in two samples (<1%). *Sphagnum* peaks twice in the zone. Charcoal is low and declining. |
| TR6  | 132-32     | *Corylus, Quercus, Calluna, Poaceae, Cyperaceae, P. lanceolata*  
The significant feature of the zone is the sustained declines for *Corylus* and *Alnus*. Poaceae and Cyperaceae expand. An increased herbaceous component is dominated by *P. lanceolata*. Cereal type grains increase in the upper samples of TR6. *Pteridium aquilinum* is the only Pteridophyte represented (5-10%). |
| TR7  | 32-0       | *Poaceae, Cyperaceae, P. lanceolata, Calluna*  
The spectra are dominated by Poaceae and Cyperaceae, with a diverse herbaceous flora. The arboreal taxa are present in low amounts. *Alnus* and *Corylus* almost disappear. Exotic coniferous pollen is present in the uppermost samples. Cereal type pollen is present in low amounts. *Sphagnum* peaks twice in this zone. |

Table 5.3  
Pollen analysis results from Tor Royal
Figure 5.9  DCA species plot of pollen data from analysis of Tor Royal sediment
(Species shown all have occurrences >1% TLP in >5 samples)

Cumulative percentage variance explained by two axes = 38.7%
Cumulative percentage variance explained by two axes = 38.7%

Figure 5.10 DCA sample plot of pollen data from analysis of Tor Royal sediment
Corylus. The transition to slightly more open conditions is indicated by the assemblage of species present in group β in which Calluna, Alnus and Poaceae together with a number of herbaceous taxa all become better represented. The last group (χ) contains species belonging to the upper levels in which a range of anthropogenic indicators are particularly well represented, including Plantago lanceolata, Cereal type grains and pollen of the coniferous plantation species (e.g. Picea).

The sample plot (Fig. 5.10) indicated a similar situation as the species plot. The basal zone was identifiable (Group I, 575 to 622cm). There appears to be a division between groups II and III, which share samples between 560 and 100cm, but display definite clustering patterns possibly indicating different pathways to the final situation in which the indicators of human activity are prevalent.

5.4.7 Interpretation of the Tor Royal pollen data

The early to mid Holocene

The basal zone (TR1) is characterised by high values for Corylus, Quercus, Betula, Ulmus and Pinus, with a diverse herbaceous flora composed of open ground indicators including Potentilla, Succisa and Rumex species, with Urtica and Hypericum perforatum-type. This zone indicates open Corylus, Betula and Quercus scrub conditions. The onset of TR1 probably dates to around 5000 BC (7000 BP) extrapolating from the \(^{14}\)C date at 574-589cm (Table 5.1). The zone appears similar to the pollen zone BLB4-BLB5 of nearby Blacklane Brook (Simmons et al., 1983) where the transition to Quercus dominated woodland is dated somewhat earlier to 7760±140 BP.

High levels of charcoal were experienced in the basal samples, which have a late Mesolithic date. This is significant since it appears that small scale disturbance was occurring at this time in other parts of the moor (Pinswell and Black Ridge Brook, Caseldine and Hatton, 1993). The site at Pinswell suggests enhanced levels of burning between 7700-6300 BP (ca. 5700-4300 BC) which led to the transformation of Corylus dominated woodland into blanket peat, with an intermediate acid grassland phase. The charcoal levels at Tor Royal suggest that burning was a widespread activity at this time and extended to these lower altitudes.

The opening of TR2 is marked by the rational limit (after Smith and Pilcher, 1973) of Alnus which is dated to ca. 7000 BP elsewhere (Simmons et al., 1983; Bush and Hall, 1987; Birks, 1989).
However, radiocarbon evidence suggest the increase of this species around Tor Royal to have occurred somewhat later, dated to 6880-6530 BP (4930-4580 BC, Table 5.1). The generally low levels and late migration of this species into upland areas of the south west has been discussed by Chambers and Price (1985). Early dates are not limited to lower lying areas elsewhere and late dates from Dartmoor and Bodmin Moor are probably a realistic representation of the regional signal (Chris Caseldine, pers. comm.). The suggestion that Mesolithic activity may have facilitated the local establishment of this species (Chambers and Price, 1985; Chambers and Elliott, 1989) is supported by the circumstantial evidence at Tor Royal. However, the relatively low *Alnus* values suggest it was only growing in restricted areas, perhaps around the margin of the developing mire.

The base of TR2 indicates a denser woodland cover, composed of *Quercus*, *Betula* and *Alnus* with *Ulmus* and *Fraxinus* likely to have been components at a lower altitude, or on the higher nutrient status soils of the slopes surrounding the mire. *Tilia* appears for the first time in this zone, although its low representation in the spectra may be due a combination of factors. It is likely to have formed a more active component in woodlands at a lower altitude, and the fluctuating size of the pollen catchment area may affect its relative abundance (Waller, 1994). In this zone *Corylus* is out competed by *Quercus*, aided possibly by Mesolithic activity.

Heathland develops for the first time during this zone, forming a major component of the vegetation at the expense of the deciduous forest cover, but also relates to a contraction in the area of grassland. *Calluna vulgaris* would most likely be restricted to the better drained areas such as the summits, slopes and forest openings, although it may have grown on the developing blanket bog initiated at about this time (Staines, 1974). The precise dating of blanket bog development of an area such as Dartmoor is not considered possible due to the varying effects of anthropogenic disturbance, and the wide differences in local topography (Maguire, 1983; Moore, 1993). Many of the features noted in other areas of the British Isles which are precursors to blanket peat initiation, including declining arboreal pollen, the use of fire and increasing acidity (Moore, 1988) are present in the Tor Royal pollen and geochemical sequences. The TR1/TR2 boundary is taken as the period when blanket peat first began development on the slopes around the bog, with a date of 4930-4580 BC.

TR3 sees a marginal recovery of *Corylus*, but *Ulmus* and *Quercus* continue to decline. Jacobi et al. (1976) working in the southern Pennines state that contemporaneous with the decline of *Corylus*, an increase in charcoal concentration is related to a permanent suppression of the closed tree cover, and
possibly hastened the onset of soil deterioration and blanket peat formation. Increased disturbance is indicated towards the TR4 boundary by an elevated charcoal concentration, a decline for Quercus and Corylus, and an expansion of herbaceous taxa indicative of open communities, e.g. Rumex species, Plantago lanceolata and Ranunculus acris-type. Increasing sedge pollen with a concurrent decrease in Calluna is probably a local on-site vegetation change, since the latter is generally insect pollinated and thus interpreted as being of local origin (Evans and Moore, 1985).

Post-elm decline changes
The Holocene Ulmus decline in the Tor Royal sequence seems to occur at 500cm close to the TR2/TR3 boundary, placing the event at around ca. 3600 BC (5600 BP), and thus indicates the position of the Mesolithic-Neolithic transition. The small increase for Poaceae at this time was similarly noted by Smith and Willis (1962) at Fallohoghy, Ireland. There the reduction of Ulmus and the expansion of grasses were interpreted as an indication of early pastoral activity, which seems likely at Tor Royal given the advent of different exploitation strategies associated with the Neolithic period (Smith et al., 1981). The reduction of Ulmus is followed ca. 1000 years later by the first significant levels of Plantago lanceolata, both features apparent in other Dartmoor pollen diagrams (Taw Head and Postbridge, Simmons, 1962; Blacklane Brook, Simmons et al., 1983; Blacka Brook, Beckett, 1981).

The expansion of Cyperaceae from 500cm may result from increased surface wetness associated with the initiation of blanket bog development, or relate to local on-site change. TR4 marks the empirical limit of Fraxinus and the reasonably consistent representation of Fagus. The occurrence of the former species at around 4500 BP is consistent with other work (Birks, 1989) but Fagus is not usually recorded until much later (1-2000 BP, Huntley and Birks, 1983; Birks, 1989; Bennett, 1989; Huntley et al., 1989). The earliest south western record is ca. 4500 BP from a Neolithic wooden trackway at Blakeway Farm, Somerset (Godwin, 1975) and the Tor Royal data support the idea that it was present further west sporadically from much earlier than is generally recognised. Comparison to other Dartmoor sites for this period is possible. At Lee Moor (275m OD) the Neolithic period is characterised by local Alnus growth, localised scrubby woodland, and a small amount of grassland with a herb flora suggesting a largely pastoral economy. The absence of heathland development is noted at this site. Blacka Brook (BB5) is similar to Tor Royal in that heathland is present, with human activity indicated by the presence of various ruderal species. Minor clearance by Neolithic
people is indicated in the profiles from Taw Head and Postbridge (Simmons, 1962, 1964b).

The British Bronze Age generally begins around 2000 BC (Godwin, 1975). This coincides with the first significant expansion of ruderal species around Tor Royal at 380cm, dated to between 2390 and 1780 BC (Table 2.1). The expansion of *Plantago lanceolata* and the sustained increase for the grasses indicate the continued importance of the area for pastoral activities. It is interesting since this is the period when the major clearance of the uplands began, but the pollen spectra from Tor Royal, although indicating continued deforestation, do not suggest more intensive activity. This may be attributable to an increased pollen source area at this time. The fact that *Alnus* is steady through the zone, and there is only a single deviation in the Cyperaceae curve suggests minimal disturbance to the local vegetation communities. The very gradual decrease of arboreal species, and replacement by grassland interspersed with *Corylus* scrub, with *Fraxinus* colonising the lower open patches indicates an imperceptible removal of woodland cover. Further evidence for the presence of open ground is confirmed by increases in *Pteridium, Potentilla* and *Rumex* species. The zone appears contemporaneous with nearby Blacklane Brook (BLB6) in which shrubs invade the more exposed areas following deforestation, accompanied by an increased weed flora component. It is significant that *Pteridium aquilinum* first becomes a component of the vegetation following the early Bronze Age clearances around Tor Royal, suggesting larger tracts of open land.

The archaeological evidence for this time confirms the suggestion that the moor was primarily utilised for pastoral activities. The mid to late Bronze Age saw an intensification in the utilisation of moorland resources culminating in the construction of extensive boundary structures, the ‘reaves’, around 1300 BC (Fleming 1978a,b, 1979, 1988; Maguire et al., 1983).

The appearance of cereal type pollen at 275cm is most likely derived from local late Bronze Age arable cultivation. Beckett (1981) states that although the level of farming at this time would have been on a minor scale, the available pollen evidence suggests as much cultivation has taken place during this time as at any time since, including the Medieval period. The low pollen productivity and dispersal capabilities of the majority of arable crops, in association with the basic harvesting techniques used may result in an under-representation of these species in the pollen record (Vuorela, 1973; Hall, 1988).
Given the radiocarbon dates it is difficult to identify the Iron Age in the Tor Royal profile with any degree of confidence. It is however suggested that the period relates to a position in the core between ca. 220-250cm. The resolution of the pollen record for this period hampers the level of interpretation, but it seems possible to reject the classically adopted archaeological hypothesis for wholesale upland landscape abandonment during this period (cf. Young and Simmonds, 1995). It appears that the extent of grassland dominated areas expands, although there is no palynological evidence for arable activity during this period. Obviously the lack of evidence may result from a number of factors including those outlined above, and do not make it possible to refute the proposition of Iron Age arable activity on Dartmoor at this time. The increased abundance of Sphagnum spores relates possibly to the deterioration of climatic conditions (Godwin, 1975; Kilian et al., 1995) frequently cited as to have caused the exodus of the moorland population (Pearce, 1978). However, recent archaeological theory has suggested the upland would have become a 'marginal farming resource' (Quinnell, 1996) during the Iron Age and later periods. This is certainly apparent from the palaeoenvironmental data obtained from Tor Royal and a number of other locations in south west England (Rough Tor on Bodmin Moor, Gearey, 1996; Gearey and Charman, 1996) covering this time frame.

**Historic landscape changes**

The Medieval period saw an increasing human population on the moor, resulting in habitation and increased arable production. Numerous examples of Medieval settlements exist on Dartmoor (Beresford, 1979; Austin et al., 1980; Austin and Walker, 1985), although there is no evidence to suggest these sites were established before AD 1200 (Allan, 1996; Henderson and Weddell, 1996). The increased levels of cereal pollen above 80cm (ca. AD 1100) corroborate this suggestion, and is likely to be linked to the widespread traces of cultivation on the upland, including characteristic field patterns with associated cultivation ridges (Fleming, 1996). The upper zones indicate a further development of grassland communities and a significant expansion of herbaceous taxa. Arboreal pollen is still declining with the indicators of open habitats expanding. It is significant to see Corylus decline dramatically, possibly relating to further selective clearance. The decline in charcoal concentration during this period suggests the minor use of fire, probably relating to small scale domestic activities.

TR7 reflects the establishment of the modern moorland landscape with a mix of open heath and grassland dominated by Calluna, members of the Poaceae and Cyperaceae families, and small
pockets of deciduous woodland on the fringes of the moor. The presence of Picea, Abies and Pinus at ca. 20cm with an extrapolated date of ca. AD 1800, relates to the establishment of coniferous plantations in the Princetown area (Simmons, 1962) and areas surrounding the site itself (Plate 5.2). Some contraction in the area of Calluna dominated heathland has occurred during this time, probably as a result of recent over-grazing or uncontrolled burning activities, as suggested by the marginally elevated levels of charcoal at 20cm. The retraction of Calluna dominated areas is a common feature of British upland heaths (Stevenson and Thompson, 1993). Their investigations reveal heather cover to have declined in ca. 90% of the sites studied over the last 200 years, attributing its demise to a range of factors including those suggested above in addition to afforestation, atmospheric pollution and climate change.

5.5 Discussion of the palaeoenvironmental development of the Tor Royal area

The geochemistry of the basal sediments suggest physical disturbance in the catchment of the mire due to increased levels of mineral matter and those elements associated with clastic material (Table 5.4). However, this material may result from bioturbation of the basal sediment incorporating fine particulate matter as sedimentation begins. The pollen record reflects open Betula-Corylus-Quercus woodland, with an open habitat herbaceous flora. Acidification of the mire and the catchment soils after ca. 4600 BC is reflected by the sediment geochemistry and the development of heathland and blanket bog. Deforestation is gradual throughout the Holocene, although there is a period of transition to more intensively managed open habitats following the Ulmus decline. Fraxinus and Fagus are both present in the woodland vegetation from the mid Holocene period.

On the basis of the geochemical data it seems possible to suggest the transition between minerotrophic and ombrotrophic conditions occurred around 1500 BC (ca. 350cm), in an environment experiencing increased disturbance by the Bronze Age population. Low levels of base elements in zones TRGa-c suggests the system was becoming progressively more acidic. This may have resulted from the increased ground cover of Calluna and associated increases in leached organic substances (e.g. polyuronic acid). Gradual increases in the ash and Si content of the sediment from 320cm suggest the increasing influence of wind-blown material produced as a result of increasing catchment disturbance activity. This may explain the elevated amounts of Ca and Na in chemizones TRGd-f. However, these elements may also relate to autogenic processes given their strong affinity for organic ligands (Engstrom and Wright, 1984). The modern influence of
<table>
<thead>
<tr>
<th>Time</th>
<th>Cultural period</th>
<th>Geochemistry</th>
<th>Vegetation</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD 1950</td>
<td>Modern</td>
<td>Significant increase in clastic elements and ash.</td>
<td>Plantation species present.</td>
<td>Grassland dominated moorland</td>
</tr>
<tr>
<td>AD 1000</td>
<td>Medieval</td>
<td></td>
<td>Cereal pollen</td>
<td>Marginal grazing resource</td>
</tr>
<tr>
<td></td>
<td>Dark Ages</td>
<td>Declining TOC</td>
<td>Reduced arboreal pollen</td>
<td>Continued utilisation of moorland resources</td>
</tr>
<tr>
<td>0</td>
<td>Romano-British</td>
<td>Increased mineral material: Si, Al, Na, Ca</td>
<td>Cereal pollen &amp; weeds</td>
<td>More open environment, much activity on moor.</td>
</tr>
<tr>
<td>1000 BC</td>
<td>Bronze Age</td>
<td>OMBRO</td>
<td>Increasing evidence for grassland communities</td>
<td>Increasing anthropogenic activity - pastoralism</td>
</tr>
<tr>
<td>2000 BC</td>
<td>Neolithic</td>
<td>MINERO</td>
<td></td>
<td>Evidence for forest clearance - charcoal</td>
</tr>
<tr>
<td>3000 BC</td>
<td></td>
<td>Increasing TOC, reduced aeration, lower Fe, pH</td>
<td></td>
<td>Blanket bog initiates in area</td>
</tr>
<tr>
<td>4000 BC</td>
<td></td>
<td></td>
<td>Closing woodland</td>
<td>Evidence for forest disturbance</td>
</tr>
<tr>
<td>5000 BC</td>
<td>Mesolithic</td>
<td>Mineral matter, high Si, Al</td>
<td>Open Betula-Corylus</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 Summary of the palaeoenvironmental development of Tor Royal, central Dartmoor

149
groundwater seems confined to the basal two metres of sediment.

No absolute geochemical evidence exists for the exploitation of the moorland mineral resources from Bronze Age times. Given the nature and resolution of the sediments from Tor Royal it was expected to gain a history of atmospheric metal pollution similar in content to those gained from other depositional environments (Livett, 1988; Van Geel et al., 1989; Hong et al., 1994, 1996; Shotyk, 1996a). The specific problems of trace metal detection using EDMA will be discussed in more detail, with reference to the results from the other site investigations and supplementary geochemical data in Chapter 9.

Final woodland decline resulted principally in the removal of Corylus, just prior to the expansion in cereal growth which reflects the Medieval period. Recent coniferous plantations date the upper sediments to around 1800 AD, but the geochemistry is too strongly affected by the active surface layer to be reliable.

5.6 Discussion
The nature of the data from EDMA and pollen analysis of these sediments is fundamentally different, particularly for the ombrotrophic sediments. Each dataset reveals information on a particular aspect of the palaeoenvironmental conditions. The geochemical signals, while affected by conditions external to the accumulating mire, are largely dependant upon autogenic processes associated with the accumulation of organic material through time. The pollen data reveal the changing nature of the vegetation at local, extra-local and regional scales (Jacobson and Bradshaw, 1981).

The increasing flux of mineral matter to the system detected after the attainment of ombrotrophic status provides an indication for increasing disturbance caused by human activity, which continues to present times. This material seems to be composed of alumino-silicate mineral associations given the correspondence between Si, Al and the ash profile. The analysis did not reveal the expected history of heavy metal deposition. This may be a factor of the low concentration of these elements in the peat matrix, and the detection capabilities of the EDMA technique. The inter-correlated nature of these profiles (with Mn) may point to their questionable utility as was noted previously in Chapter 4. Further analyses from the other sites may clarify this feature.
Once again a number of elements proved of little use in the investigation of palaeoenvironmental processes possibly due to the same problems outlined above for the heavy metals. Potassium only displayed useful information in the uppermost sediments, as a result of bio-accumulation processes within the acrotelm (Aulio, 1980), but was absent from the underlying sediments. Shotyk (1988) notes this element to exhibit a low humic/fulvic acid complexing capability and as such is readily leached from acidic peatland systems. P also produced information that was difficult to interpret in terms of palaeoenvironmental processes, due to the large standard errors associated with detected peaks. The fluxes of P in the uppermost sediments relates most likely to the changing conditions in the acrotelm layer of the system.

It seems in this instance that palynological investigation of the sediments from this site yield far more useful information with respect to the palaeoenvironmental history of the area, given the apparent limitation of the EDMA technique. The next chapter presents further analyses from the granitic upland of Dartmoor. The site is in a very different environmental context and as such was hoped to reveal new information about the effectiveness of EDMA to elucidate palaeoenvironmental processes and activity at a smaller spatial scale.
Chapter 6
Upper Merrivale, western Dartmoor.

6.0 Introduction

This chapter presents the results gained from geochemical and palynological analysis of a small soligenous mire in the upper reaches of the River Walkham catchment, western Dartmoor (Fig. 6.1). The justification for selecting this site is outlined below:

(i) the sediments have accumulated in a different environmental situation to any of those presented so far and reveal information about the utility of EDMA in this type of sedimentary environment. Using these data the different processes affecting the retention and mobility of elements may be detected.

(ii) The enclosed local topography (Plate 6.1) results in a pollen source area dominated by local and extra-local components (Jacobson and Bradshaw, 1981). This is useful since it will provide information at a local scale, detailing vegetation dynamics which relate to landuse change in the immediate locality.

(iii) The site is located adjacent to a 17th century tin blowing and stamping mill (Plate 6.2) which has been the focus of recent archaeological excavation by the Dartmoor Tin-working Research Group (Gerrard and Greeves, 1992, 1993; Greeves 1994; Greeves and Newman, 1996). It therefore provides the opportunity to examine the evidence for this activity in the sedimentary record.

(iv) The site lies in one of the best preserved prehistoric landscapes of mainland Britain (Butler, 1991), with the impressive stone rows of Merrivale ca. 2km to the south, and extensive evidence for Bronze Age hut circle settlement and prehistoric land boundaries. The site therefore provides an opportunity to investigate the activities associated with the numerous phases of human exploitation in this part of the Dartmoor landscape.

The site provides detail on a different scale to that obtained previously from Tor Royal, concentrating more specifically on the evidence for human modification of this part of the Walkham catchment.

6.1 Site location, morphology and modern vegetation communities

Upper Merrivale (SX 552766) is located 4.5km north west of Princetown at a height of ca. 340m.
Calm
Hut circle settlements
Old tin workings
River / leat
Spot height
Contour (metres)
Spot height
Boundary work 'reaves'

Figure 6.1 Location of Upper Merrivale sampling location
Plate 6.1 The Upper Merrivale catchment, sampling site marked by an arrow.

Plate 6.2 The Upper Merrivale blowing and stamping mill in the foreground. The sampling site is located on the opposite side of the river.
The sampling site is located in a valley between the slopes of Great Mis Tor to the east and Roos Tor to the west (Fig. 6.1, Plate 6.1). The vegetation of the surrounding slopes is characterised by grassland communities composed largely of Agrostis tenuis, Festuca ovina, Galium saxatile, Luzula campestris and Pteridium aquilinum (Ward et al., 1972), although the sampling site itself is dominated by Juncus spp., Molinia caerulea, Sphagnum spp. with isolated occurrences of Calluna vulgaris, Erica tetralix and Hydrocotyle vulgaris.

The site extends for ca. 75m along the eastern bank of the River Walkham and is fed directly from springs draining the slopes of Great Mis Tor. This site was chosen since it was the largest of a number of similar systems, but was closest to the evidence for historic tin processing activity. Depth probing of the mire confirmed the deepest section to be 141cm.

6.2 Archaeology of the Upper Walkham catchment

The earliest evidence for a human presence in the area are the stone rows at Merrivale, although these structures remain undated. The only dating evidence is the fact they apparently lack association with later beaker graves and cists in the same region (Todd, 1987). Emmett (1979: 107) concludes:

"At present the only conclusion to be drawn is that the construction, extension and abandonment of the stone rows occurred between the late Mesolithic clearances and the later Bronze Age."

Much discussion has been directed towards the evidence for settlement and palaeoeconomy in the area, which dates generally from the mid to late Bronze Age. It appears the different structural styles of settlement may be attributed chronologically to different time periods. Walled pounds indicate the early Bronze Age incursion of pastoralists into previously unoccupied regions. The mid Bronze Age experiences an expansion of settlement during which the pounds are replaced by large open villages with increasing indications of arable activities. Late Bronze Age times are characterised by a reduction in settlement size and a general movement of permanent settlements to the moorland fringe (Hamond, 1979; Price, 1993), with possible re-use of earlier pounds as seasonal or short term dwellings associated with transhumance practices (Radford, 1952). Evidence for all of these structural styles are seen in the area immediately surrounding the sampling site on Langstone Moor, around Great Mis Tor and at Merrivale Bridge East (Butler, 1991). Particularly well preserved features relating to Bronze Age pastoral and arable activity are the earthen bank features known as reaves. These once formed substantial banks dividing areas of the moor into discrete territorial units.
The reaves separate the moor into two main landscape categories. Large parallel systems demarcate enclosed land with some indication of arable activity, with a higher altitude zone of unenclosed grazing land between the watershed reaves (Fleming, 1979, 1988). The reaves are generally viewed as a response to increased pressure on land resources during the late Bronze Age, around 1700 BC (Fleming, 1988).

Evidence for Iron Age activity on Dartmoor is sparse, with only a very few examples of settlements confined largely to the upland fringe. However, a postulated Iron Age enclosure exists at White Tor, to the north of the sampling site (Fig. 6.1), although its contemporaneity with the other forts of the period is questioned by the different construction styles. However, this may be due to its geographical location with an abundance of readily available stone for building purposes (Brailsford, 1938).

An archaeological hiatus exists for the next ca. 1000 years during which time no direct evidence for settlement can be seen in the area. Shillapark Farm is perhaps the earliest settlement of the historic period in the area, which displays a classic curvilinear comditch, and has buildings orientated downslope - a characteristic displayed by virtually all Medieval longhouses. The later remains in the catchment are dominated by tin working features dating from perhaps the mid 12th to the second half of the 19th centuries (Greeves and Newman, 1996). The tin blowing and stamping mill adjacent to the site was operational during the 16th and 17th centuries (Greeves, 1994).

6.3 Sampling regime

Samples were collected using a standard Russian auger (50cm x 5cm). Two samples were taken for radiocarbon dating (Table 6.1). Each monolith extracted was described in the field using Troels-Smith (1955) classification and subsequently re-examined in the laboratory to confirm initial descriptions (Fig. 6.2). A total of 28 samples were taken from the profile at 5cm intervals and prepared for EDMA, pollen, Total Organic Carbon analyses and ashing at 900°C (Aaby, 1986; Shotyk, 1996b).

6.4 Palaeoenvironmental reconstruction of Upper Merrivale, western Dartmoor

Discussion will initially be directed towards the stratigraphy of the sediment followed by the results from both geochemical and palynological investigations. Multi-variate techniques were applied to
Very fibrous felted unit, modern Cyperaceae stems and root material evident
nig.2 elas.3 sicc.1 humo.0 Th2 Dg2

Light brown, compact felted unit with Calluna vulgaris rootlets evident. Grades into next unit over ca. 20cm.
nig.2 elas.3 sicc.3 humo.0/1 Th2 Dh1 Dg1

Dark brown, well humified silty peat with small mineral particles visible. Few macrofossil remains evident, but increasing Cyperaceae stems to base of profile.
nig.3 elas.0 sicc.3 humo.4 Sb3 Dg1 As+ Di+(lignum)

Abundant mineral particles at this level

Wood fragments

Figure 6.2 Stratigraphy of the Upper Merrivale sediment
both sets of data, the results from which will be discussed shortly.

6.4.1 Stratigraphic description of the sediment

The basal sediment is composed of a well humified greasy unit with very occasional macrofossil remains, but with increasing Cyperaceae stems to the base. The overlying unit is composed of well humified material with an homogenous structure and no identifiable macrofossil remains. This grades into a unit (50-100cm) composed of homogenous material, with fragments of charcoal and small mineral particles, which appear more abundant in the next section of the profile. The upper sediments display little variation except for a transition to a more felted structure and the increasing presence of rootlet material, possibly of Calluna vulgaris. The most significant aspect of the sediment stratigraphically is the presence of a considerable concentration of mineral particles at 100cm.

6.4.2 Radiocarbon dating procedures and results

As already stated two samples were taken from the profile and submitted to Beta Analytic for AMS analysis. The table below gives details of the results obtained:

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Lab-code</th>
<th>$^{14}C\text{age}$</th>
<th>Calibrated age (BP)</th>
<th>Calendar age (ref AD 1950)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65-66</td>
<td>Beta-97050</td>
<td>1090±60</td>
<td>1130-920</td>
<td>AD 820-1035</td>
</tr>
<tr>
<td>100-101</td>
<td>Beta-93819</td>
<td>2230±60</td>
<td>2345-2090</td>
<td>395-140 BC</td>
</tr>
</tbody>
</table>

Table 6.1 Radiocarbon dates from Upper Merrivale

The data suggest the rate of sediment accumulation between 65 and 100cm was 0.021 cmyr$^{-1}$. It is not possible to extrapolate with any degree of certainty beyond this. However, given the increasing levels of Alnus pollen at 125cm a date of 4930-4580 BC is suggested by comparison with the Tor Royal profile (Table 5.1). This suggests an accumulation rate of 0.0056 cmyr$^{-1}$ between 100 and 125cm, and obviously creates considerable problems in interpretation of Neolithic and Bronze Age activity in the area since the very slow accumulation rate and/or very compressed nature of the sediment for these periods has reduced the temporal resolution of the sediment; a period when much activity is inferred from the archaeological evidence. Assuming the exotic coniferous pollen detected
in the uppermost sediments \textit{(Abies, Picea and Pinus)} is due to plantations of the last two centuries an accumulation rate of ca. 0.06 cm yr$^{-1}$ is feasible for the upper sediments.

In a sedimentary situation such as the one at Upper Merrivale in which there is much field evidence for the influence of human activities from an early date the presence of a hiatus in the depositional record is always a possibility. It is possible that the profile may have been truncated in late Neolithic times although more radiocarbon dating evidence from these levels is required to investigate this further.

6.4.3 EDMA investigation

Initially it was hoped that geochemical analysis of the sediments from Upper Merrivale would reveal a record of local mineral exploitation associated with the tin streaming and processing activities in the area. The possibility also existed for the identification of prehistoric tinning signals, suggested to have occurred in the immediate vicinity (Greeves and Newman, 1996). The investigation was also aimed at elucidating wider scale palaeoenvironmental processes, such as the geochemical consequences of local deforestation and the subsequent degradation of catchment materials through the initiation of retrogressive pedogenic processes.

EDMA geochemical results are presented as elemental profiles (Fig. 6.3a/b) divided into six distinct chemizons (section 2.4.1). The chemizons are described in Table 6.2. Initial observations question the utility of a number of elemental profiles. The heavy metal elements (As, Pb and Sn) along with Mg and Mn all display very low values throughout the core. They also behave in a very similar fashion, a feature observed for the other sites so far discussed. This close relationship between profile features may point to the fact that these elements are of no use, and the profile characteristics are therefore a result of fluctuations in the other, more abundant elements. However, the peak exhibited by Sn, As, Pb at 100 cm may suggest caution is required before discounting the use of these elements. Na and Ca display generally stable profiles, with only one peak each. Their general absence may be a function of the sedimentary system, relating to increased levels of acidity which favours mobility and removal of these elements through leaching processes (Goldschmidt, 1954; Shotyk, 1988).
Depth (cms below ground surface)
Si and Al dominate the zone. Steady state equilibrium is displayed for a number of elements: the trace metals Pb, Sn, As with Fe, Mn, Na, K and Mg. P peaks at the MVLGa/b boundary, whilst S falls consistently. Ca exhibits a peak at 130cm of ca. 5%. TOC is high and stable at 35%. Mineral content of the sediments in MVLGa is around 10%.

Sn, As and Pb all display gradual increases through the zone with a peak value for these traces found at 100cm. A similar profile is presented for Fe, K and Si. S, Al and TOC fall through the zone and exhibit dynamic equilibrium conditions at 100cm. Na and Ca are steady.

Increasing levels of Si and TOC are accompanied by declining profiles for Al, K and mineral material. Fe also declines following a peak at 95cm (2%). The trace elements appear intercorrelated and stable, except for Sn which declines from the peak experienced at the MVLGb/c boundary. S behaves erratically, but displays a profile similar to TOC.

The zone is dominated by Si, which at the upper boundary reaches ca. 80%. Al declines steadily through this zone. Na, K, Ca and Fe appear only in trace quantities. S and Cu are low and stable. The trace elements display intercorrelated profiles with Mg and Mn.

Ca, K, Na, Fe all display very low amounts of <1%. P and Al display similar profiles in this zone. The peak of these elements at 35cm is associated with a reduced Si content of the sediment, and declining levels of mineral material. The trace metals display very similar profile features.

Si dominates the elemental spectra of this uppermost zone, peaking with a surficial value of 80%. Al, Cu, S, Fe, Na, K and Ca are present only in small amounts. The trace elements are intercorrelated and fluctuate widely in this zone.

<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVLGa</td>
<td>141-125</td>
<td>Si and Al dominate the zone. Steady state equilibrium is displayed for a number of elements: the trace metals Pb, Sn, As with Fe, Mn, Na, K and Mg. P peaks at the MVLGa/b boundary, whilst S falls consistently. Ca exhibits a peak at 130cm of ca. 5%. TOC is high and stable at 35%. Mineral content of the sediments in MVLGa is around 10%.</td>
</tr>
<tr>
<td>MVLGb</td>
<td>125-100</td>
<td>Sn, As and Pb all display gradual increases through the zone with a peak value for these traces found at 100cm. A similar profile is presented for Fe, K and Si. S, Al and TOC fall through the zone and exhibit dynamic equilibrium conditions at 100cm. Na and Ca are steady.</td>
</tr>
<tr>
<td>MVLGc</td>
<td>100-75</td>
<td>Increasing levels of Si and TOC are accompanied by declining profiles for Al, K and mineral material. Fe also declines following a peak at 95cm (2%). The trace elements appear intercorrelated and stable, except for Sn which declines from the peak experienced at the MVLGb/c boundary. S behaves erratically, but displays a profile similar to TOC.</td>
</tr>
<tr>
<td>MVLGd</td>
<td>75-45</td>
<td>The zone is dominated by Si, which at the upper boundary reaches ca. 80%. Al declines steadily through this zone. Na, K, Ca and Fe appear only in trace quantities. S and Cu are low and stable. The trace elements display intercorrelated profiles with Mg and Mn.</td>
</tr>
<tr>
<td>MVLGe</td>
<td>45-30</td>
<td>Ca, K, Na, Fe all display very low amounts of &lt;1%. P and Al display similar profiles in this zone. The peak of these elements at 35cm is associated with a reduced Si content of the sediment, and declining levels of mineral material. The trace metals display very similar profile features.</td>
</tr>
<tr>
<td>MVLGf</td>
<td>30-10</td>
<td>Si dominates the elemental spectra of this uppermost zone, peaking with a surficial value of 80%. Al, Cu, S, Fe, Na, K and Ca are present only in small amounts. The trace elements are intercorrelated and fluctuate widely in this zone.</td>
</tr>
</tbody>
</table>

Table 6.2 Description of chemizones from Upper Merrivale
Figure 6.4 DCA element plot of EDMA data from Upper Merrivale, western Dartmoor
Cumulative percentage variance explained by two axes = 77.6%

Figure 6.5 DCA sample plot of EDMA data from Upper Merrivale, western Dartmoor
Multi-variate analysis of the Upper Merrivale EDMA data

The DCA plots of the geochemical data are shown in Figs. 6.4 and 6.5. Investigation suggests a relationship between %ash and the Si content of the sediment, as such this indicates that axis one represents the division between mineral matter and organic material, since S is located some distance from these clastic components. The position of Ca may therefore suggest its geochemistry in this situation is largely controlled by autogenic processes. It also seems likely that the presence of Al is not primarily governed by the levels of alumino-silicate material, as such it may be related to the presence of humic material, since Engstrom and Wright (1984) comment that Al can be chelated with high molecular weight humic materials. Axis two seems to indicate the pH regime of the system. A clustering of elements towards the upper limit of the axis, composed of Na, K and Fe, suggests these elements to be associated with a higher base status, as opposed to TOC and Cu which in this case are associated with acidic, anaerobic processes. The sample plot (Fig. 6.5) is clearly divisible into two distinct groups, which relate solely to the pre- and post-100cm event. The specific nature of this event will be discussed in the following sections.

Interpretation of the geochemical signals from Upper Merrivale

The initial status of the system

The indicators of physical erosion (Na, K, Mg, %ash) are all low and stable. The basal zone seems to suggest stability in the catchment. However, evidence to suggest increasing disturbance to MVLGb is presented by the falling S and TOC profiles. This may be significant since both are important elements associated with the metabolism of all living organisms (Goldschmidt, 1954). The peak of P at 125cm may be associated with inorganic clastic minerals or result from increased precipitation of the element with organic matter (Engstrom and Wright, 1984). The former is unlikely since there is limited evidence for the inclusion of clastic minerals into the sediment at this time. The single peak of Ca at 130cm may relate to mechanical erosion of catchment material, but the element is more easily removed in solution from mineral material than K, Mg and Na, which are absent at this level. Ca has a strong affinity for organic ligands, as such the signal at 130cm may relate to autogenic processes within the sedimentary body (Engstrom and Wright, 1984). The absence of Fe in MVLGa potentially suggests acidic, anaerobic conditions.

The geochemistry of Cu here may be linked to the formation of sulphides in the anaerobic zone since the presence of sulphate ions and organic matter can lead to the microbial formation of H$_2$S, and
thus to the precipitation of metal sulphides (Goldschmidt, 1954). The presence and behaviour of Cu in MVLGa seems most likely controlled by a combination of sulphate reduction and the formation of metal/organic complexes (Livett et al., 1979; Hermann and Neumann-Mahlkau, 1985; Shotyk, 1988; Stewart and Fergusson, 1994).

Increasing catchment disturbance

The signals associated with MVLGb present more clearly an episode of environmental disturbance into which quartzitic grains were introduced to the sedimentary system at 100cm. This explains the peak in Si, K and %ash. Elevated values for the heavy metals at this level suggest possibly that the mineral material was enriched in these elements. The disturbance may therefore have been connected with prehistoric mineral extraction procedures; although the radiocarbon evidence produced a date of 395-140 BC (Table 6.1), a period generally considered to indicate the demise of Bronze Age traditions and the onset of Iron Age times. It must be stated that the link between the geochemical evidence and the archaeological hypothesis of prehistoric tinning activity in the area is tentative. As has already been stated the utility of EDMA for heavy metal analysis from this type of sedimentary environment seems questionable. Further investigation is required in a range of different environmental situations with comparison made to the results from a comparable geochemical technique.

The gradual increase for Si and K suggests intensifying activity from MVLGa, possibly caused by increasing landscape disturbance, which may have taken the form of mineral extraction or deforestation activities. The sharp decline for S and TOC at 100cm confirm intensive disturbance to the peat accumulating system at this time. The decrease in TOC may relate to the erosion of the peat body itself, and general degradation in catchment and mire materials. Increasing Fe from 105cm may suggest the system was becoming less acidic and experiencing increased periods of aeration, possibly even drying out since Fe is considered ubiquitous in oxygenated environments (Goldschmidt, 1954; Mackereth, 1966; Jones and Bowser, 1978; Engstrom and Wright, 1984; Naucke et al., 1993). However, the increased Fe content of the sediments at this level may not result from a change in the internal status of the mire, but from the increased transportation and deposition of inorganic oxides and oxide coatings on mineral material. The elevated levels of mineral material (%ash) at 100cm exceed the generally accepted values for fen peat reported by Naucke (1980), suggesting the bulk of this material was deposited as suspended matter carried locally by the river or in the spring waters.
This increased runoff may have been the result of increased woodland clearance on the surrounding slopes, or a possible climatic change.

The system appears to recover following the disturbance of MVLGb. However, it seems likely that it never attained its pre-disturbance status: S, TOC and Al exhibit dynamic metastable equilibrium at 100cm suggesting a major environmental change (Butzer, 1982; Grattan, 1994). The heavy metal elements decline marginally from 100cm then attain static equilibrium for the rest of the zone. Both K and Mg fall through MVLGc suggesting a declining input of base rich material and/or enhanced leaching under increasingly acidic catchment conditions. This is confirmed by the declining levels of Fe from 95cm upwards, which is mobilised under acidic, anaerobic conditions. Si fluctuates through the zone, exhibiting an overall increase and does not display a relationship to the Al profile, which suggests a possible link with organic material, as opposed to an association with alumino-silicate material (Muscutt et al., 1993). The presence of diatoms at 95cm was confirmed by SEM investigation, thus the Si and ash signals contain both biogenic and allogenic components. The elevated levels of P in MVLGc may relate to the presence of diatoms in the sedimentary system since this element is considered one of the controlling variables for the organisms (Goldschmidt, 1954; Engstrom and Wright, 1984; Grattan, 1994).

Post disturbance conditions

Increased acidity is suggested from MVLGc since a number of elements exhibit a very low presence in this zone (Ca, Mg, K, Na and Fe). However, the signals associated with MVLGd indicate general stability with an absence of elemental peaks. Many of the elements display declining trends through this and the remaining zones, including S, P, Al, Mg, K and the heavy metal elements, indicating a continued degradation of catchment materials, possibly initiated by the earlier disturbance phase. The presence of diatoms was again noted at 70cm and possibly explains the high levels of Si in MVLGd. The Si and Al elemental curves display inverse profiles, as such it is unlikely they relate to the presence of alumino-silicate material, however it may be the case that the Al has experienced post-depositional leaching partially obscuring the palaeoenvironmental signal for the element.

Signals associated with the intense tinning activity inferred from the concentration of industrial archaeology in the area appear to be absent. Given the accumulation rates discussed above (section 6.4.2) sediments at a depth of 20cm date from the 16th/17th century. This is the period when the tin
mills in this area were operating at capacity (Greeves and Newman, 1996). The minor peak for Sn, As and Pb may be attributable to such activity but caution must be used in the interpretation of these signals as stated earlier.

Modern signals
This upper zone is complex to interpret due to the combination of active chemical, biological and physical mire processes and the signals of recent environmental change. The acrotelm/catotelm boundary seems to be located at 20cm due to the bio-accumulation of K above this level in the active acrotelm layer, and the possible concentration of heavy metals accumulated at this boundary. Si and Al display steady state equilibrium which suggests constant supply of these elements to the sediment.

6.4.6 Pollen analysis of the sediments from Upper Merrivale
The nature of the peatland system and its topographic setting suggest that taphonomic processes will result in pollen spectra dominated by local and extra-local components (Jacobson and Bradshaw, 1981; Prentice, 1985), with a potentially large amount of pollen entering the system as components of run-off (Chen, 1988). The effects of human activity therefore form the focus of palynological investigation here. The results are presented as a pollen diagram (Fig. 6.6) and described in Table 6.3. The data are presented as percentages of Total Land Pollen (TLP). The DCA plots from analysis of the pollen are presented as Figs. 6.7 and 6.8.

6.4.7 Multi-variate analysis of the Upper Merrivale pollen data
DCA of the pollen data indicate a number of discrete species groupings (Fig. 6.7). The first (group α) is indicative of a woodland habitat, composed of Quercus, Betula, Alnus and Salix with epiphytic species, including Polypodium and other components of Pteropsida undiff. This group is present in the basal levels of the core and points to the initial status of the local vegetation. The next group (β) includes species typical of disturbed habitats (Plantago lanceolata, Rumex undiff. and Pteridium aquilinum) possibly indicating the vegetation response to the activity identified geochemically and stratigraphically at 100cm. The change in the nature of the local vegetation suggests the activity to have been local but relatively intensive. Group χ contains those species associated with acidic grassland communities, as identified for other areas of Dartmoor (Hatton, 1991; Caseldine and Hatton, 1993) and includes such taxa as Potentilla, Lotus, Succisa pratensis and members of the Asteraceae family. This group indicates the post disturbance condition of the local area. The final
Figure 6.6
Upper Merivale percentage pollen diagram
Exaggeration factor x 10, + indicates a trace occurrence (<1% TLP)

Calendar years (2 sigma)

Depth in cms

Poaceae
Poaceae +40 microns
Cyperaceae undiff.
Plantaginaceae undiff.
Plantago lanceolata
Ranunculus acris-type
Sinapis-type
Urtica dioica
Chenopodiaceae
Caryophyllaceae
Rumex undiff.
R. acetosella
R. acetosa
Hypericum perforatum-type
Primula veris-type
Lysimachia vulgaris-type
Resoaceae undiff.
Filipendula
Potentilla-type
Lotus
Epilobium-type
Apiaceae
Lamiaceae undiff.
Stachys-type
Rubiaceae
Valeriana officinalis
Succisa pratensis
Scabiosa columbaria
Cardueae/Asteroideae undiff.
Cirsium-type
Centaurea nigra
Lactuceae undiff.
Solidago virgaurea-type
Artemisia-type
Achillea-type
Unidentified

Analysis: Steve West

MVLP1
MVLP2
MVLP3
MVLP4Pa
MVLP4Pb
MVLP5
MVLP6
LRAZ
<table>
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<tr>
<th>Zone</th>
<th>Depth (cm)</th>
<th>Characteristic pollen types</th>
</tr>
</thead>
</table>
| MVLP1      | 140-125    | *Corylus avellana*-type, Cyperaceae, Pteropsida  
Increasing ferns through this zone (50-80%). Arboreal pollen (AP) is consistently represented, decreasing slightly to MVLP2. *Salix* increases through the zone, while *Corylus avellana*-type falls gradually. Herbaceous pollen is abundant (ca. 40% TLP) and is dominated by the sedges, with contributions from *Ranunculus acris*-type, *Rumex* spp., *Filipendula*, Potentilla-type, *Lotus* and members of the Apiaceae family. |
| MVLP2      | 125-110    | *Alnus, Corylus avellana*-type, Poaceae, Cyperaceae, *Sphagnum*, Pteropsida  
AP increases to 50% TLP, the major component of which is *Alnus*. The other trees decrease gradually to MVLP3. *Calluna* and *Poaceae* reach their empirical limit at 125cm. *Cyperaceae* pollen decreases to MVLP3. Herbaceous taxa still form a major component, with *Plantago lanceolata* appearing for the first time at 120cm. |
| MVLP3      | 110-90     | Poaceae, Cyperaceae, *Alnus*, Pteropsida  
Declining AP. Ferns increase dramatically through the zone. *Sphagnum* rises steadily. Herbaceous pollen is dominated by Poaceae and Cyperaceae, the latter declining steadily through the zone, with increasing contributions from open grassland and disturbed environment indicators. |
| MVLP4/a/b  | 90-45      | Poaceae, Cyperaceae, *Alnus, Corylus avellana*-type, *Sphagnum*  
AP falls steadily through this zone, with *Quercus* and *Betula* falling to trace amounts at 60cm. *Fagus* appears for the first time at 75cm. The shrubs are consistently represented in the zone, with *Calluna* exhibiting a maximum occurrence at 60cm. *Poaceae* increases through the zone, with Cyperaceae steadily present. Herbaceous taxa are generally well represented in this zone. |
| MVLP5      | 45-25      | Poaceae, Cyperaceae, *Alnus, Corylus avellana*-type, *Calluna*  
Poaceae increases steadily through the zone, while the arboreal species remain generally constant. Herbaceous taxa are composed largely of acidic grassland indicators. |
| MVLP6      | 25-10      | Poaceae, *Rumex* species, Cyperaceae, Pteropsida  
For the large part all of the components of the pollen spectra are constant. The only arboreal species to decrease is *Alnus* (10 to 5%). There is a consistent presence of *Fraxinus* in this zone (3%). Herbaceous components are dominated by the grasses, but the *Rumex* species increase to a peak in this zone. The indicators of acid grassland are also prevalent here. Cereal type pollen grains increase. Species attributable to the plantation of exotic coniferous woodlands are located in the upper sediments. |

Table 6.3 Description of local pollen assemblage zones from Upper Merrivale
Cumulative percentage variance explained by two axes = 57.7%

Figure 6.7 DCA species plot of pollen data from analysis of Upper Merrivale sediment
(Species shown all have occurrences >1% TLP in >5 samples)
Cumulative percentage variance explained by two axes = 57.7%

Figure 6.8 DCA sample plot of pollen data from analysis of Upper Merrivale sediment
group (δ) relates to the modern pollen spectra of the area, with components derived from a wider catchment area (*Fagus sylvatica* and *Fraxinus excelsior*).

The DCA plot of pollen sample scores (Fig. 6.8) revealed a clear pattern of groups each significantly different to produce five distinct assemblages. Group I includes the basal samples from 141 to 115cm, therefore relating to group α (Fig. 6.7). The next set includes samples covering the major signals associated with the disturbance event at 100cm (100 to 75cm). Groups III and IV include samples from post disturbance levels and thus relate to group χ of Fig. 6.7. The final sample assemblage outlines the uppermost samples, and indicates the modern vegetation communities as illustrated by group δ on the species plot (Fig. 6.7).

### 6.4.8 Interpretation of the Upper Merrivale pollen data

**The initial stage: ca. 6000-5000 BC**

The basal sediments indicate a *Corylus*, *Quercus*, *Betula* and *Ulmus* dominated woodland, in which ferns are abundant, suggesting open patches in the woodland cover. High values for *Corylus* at this time (>30% TLP) suggest it to have been present very close to the sampling site. It is likely that the river area would have been dominated by *Salix* species and members of the Cyperaceae family, with *Betula* possibly forming a component of this carr community. The ferns may also have shared this damp area, as would *Lysimachia vulgaris*-type and *Filipendula* with fen species of the Chenopodiaceae and Caryophyllaceae families. This site was more sheltered than some of the other contemporaneous Dartmoor sites (Blacklane Brook, Simmons, 1962, 1964; Simmons *et al.*, 1983; Black Ridge Brook, Caseldine and Maguire, 1986), and has fewer heathland components, higher AP/NAP ratios (40%) and a higher representation of species usually confined to the lower slopes e.g. *Ulmus*, *Hedera helix* and *Lonicera periclymenum*. The basal samples seem likely to date to the late Mesolithic/early Neolithic period, although further radiocarbon dating evidence is required to substantiate this.

The herbaceous pollen indicate the presence of open disturbed conditions, with such species as *Rumex*, *Epilobium* and *Urtica dioica*. The absence of grass and *Calluna vulgaris* pollen suggests this zone predates the inception of blanket peat for this part of the Walkham catchment. It seems likely that the high levels of *Corylus* compared to *Quercus* suggests the presence of hazel scrub, with
oak as a secondary species, although the differential pollen productivity of the two species may be a factor (Anderson, 1970). The absence of ericaceous species at this time may be explained partly by the dominance and increased shading produced by the dense Corylus avellana scrub, although the pollen dispersal capabilities of Calluna vulgaris suggests this absence may be explained by plants at some distance from the sampling site (Evans and Moore, 1985).

A changing landscape: the inception of Alnus woodland and grassland communities - ca. 5000 BC

The most striking feature of MVLP2 is the sudden, rapid rise of Alnus, usually taken as a well defined regional chronozone dated to ca. 7000 BP (Simmons et al., 1983; Chambers and Price, 1985; Birks, 1989). The greater representation of this species here in comparison to Tor Royal (Chapter 5) suggests it was actively growing as the dominant fen carr species having outcompeted Salix. It appears to have formed a closed canopy woodland which outshades the sedges, ferns and other mire components.

This zone displays the first indications of anthropogenic disturbance in the Walkham catchment. Many of the arboreal species are declining, while the pollen spectra indicates an opening of the previous woodland phase. Poaceae first becomes a component at this level as does Calluna vulgaris and Potentilla-type, with other herbaceous taxa indicative of more open conditions: Plantago lanceolata, Ranunculus acris-type and Rumex species. This suggests the onset of blanket bog development on the surrounding slopes. It is possible, given the evidence described above, to suggest that the local environment at this time became considerably wetter, indeed Sphagnum species first appear at 125cm. The triggering mechanism for the inception of blanket peat therefore seems to have been a change in local hydrological conditions (Staines, 1974; Maguire, 1983), possibly following a subtle climatic change or deforestation (cf. Chambers and Price, 1985) resulting in a greater amount of run-off (Moore, 1988, 1993).

The decline in AP and Corylus avellana with an increase in charcoal concentration points to increasing human activity in the area, although there is no archaeological evidence to support this hypothesis in the immediate area at this time. The limited dating evidence suggests this activity could well have been contemporary with other Mesolithic/Neolithic activity on the moor, e.g. Tor Royal (Chapter 5), at Pinswell (Caseldine and Hatton, 1993, 1996), and at Post Bridge and Taw Marsh (Simmons, 1962). All of these sites share common features at this time including suppression of the woodland cover, expanding levels of

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herbaceous taxa and increased levels of microscopic charcoal. Zvelebil (1994) comments that the incidence of clearing and burning phases at this time were too high to be simply explained by acts of nature alone. He suggests that deliberate forest clearance and the maintenance of more open landscapes were part of a promotional strategy to increase the productivity of nut and fruit trees and shrubs, wetland plants and possibly even native grasses. This notion suggests that increases for Corylus were possibly the result of human intervention (Smith 1970; Simmons, 1993).

Salix was outcompeted by the invasion of Alnus in MVLP2, most likely due to the effective reproductive strategies of the former which are greatly enhanced by the presence of flowing water (McVean, 1953). Chambers and Elliott (1989: 548) comment that "disturbance ....... may be regarded as a prerequisite for the expansion of alder at many sites". Given the time frame this seems a distinct possibility. Continued suppression of the local woodlands is noted in this zone with the reduction of a number of arboreal species after ca. 5000 BC. The herbaceous taxa indicate more open conditions, with an expansion of blanket bog which may relate to the increasing use of fire. Supposing there was a connection it may follow the model of environmental change proposed by Caseldine and Hatton (1993) for the Pinswell site, and by Jacobi et al. (1976) for sites in the Pennines.

Given the temporal resolution of the mid profile sediments it is not possible to clearly identify the position of the Ulmus decline with any certainty more than to say it seems to be located around 110cm, thus dating these levels to ca. 3000 BC. The very compressed nature of these sediments obscures the palaeoenvironmental information relating to the Neolithic and Bronze Age utilisation of the moorland. There is abundant archaeological evidence in the vicinity for the activities of the Bronze Age population including various types of hut circle settlement, reaves and possibly some of the ritual monuments to the south. Evidence from other parts of the upland suggest increased clearance and habitat disturbance during this period. At Holne Moor (Maguire et al., 1983) and Shaugh Moor (Beckett, 1981; Smith et al., 1981) after ca. 1200 BC increased levels of anthropogenic activity in the local area are inferred from the changing pollen spectra, and by the construction of a number of reave structures in these areas. The general character of the vegetation in these areas was probably comparable to that of Upper Merrivale at this time, dominated by Alnus with Quercus, Betula and Corylus avellana with a herbaceous flora composed of ruderal plants including Plantago lanceolata, Rumex species and Ranunculus acris-type. However, both of these
sites include indicators of arable activity which are absent from Merrivale, possibly suggesting the higher altitude sites were not as favourable during these times for cereal production, although the pollen dispersal capabilities of cereal crops may be a factor (Vuorela, 1973; Hall, 1988). The sporadic occurrence of blanket bog indicators across the moor at this time suggests that local topography and hydrological regimes dominated the triggering and development of these systems (cf. Maguire, 1983).

Increasing deforestation activity: post 500 BC

MVLP3 is characterised mainly by falling Alnus values which seem to relate to selective clearance of the species from the carr woodland. The opening of the previously dense woodland allows secondary colonisation of Salix and Betula species to occur. Similarly the ferns and sedges respond rapidly to the more open conditions. Expansion of blanket bog is also experienced.

Grasses increase through the zone, as do the indicators of open grassland communities: Potentilla-type, Lotus, Centaurea nigra and members of the Lactuceae tribe. Similarly disturbed ground indicators are significant in this zone, P. lanceolata, Urtica dioica, Rumex species and Hypericum perforatum-type. A peak of charcoal at 105cm seems to have had a significant effect on the area around the sampling site, leading possibly to an acceleration in the rate and extent of blanket bog development and recession of the forest cover, with a subsequent expansion of herbaceous species. A short-lived recovery of Alnus occurs at 95cm (ca. AD 200), but its continued decline seems to relate to a second phase of burning activity, with a further expansion of fern species, and an expansion of blanket bog.

Many of the trees expand slightly following the disturbance of MVLP3. Quercus, Betula and Corylus avellana increase, most likely forming woodland patches on the hillslopes. Alnus and Salix are present and form a secondary woodland carr in the damper area surrounding the River Walkham. The area of grassland expands through MVLP4a, with open/disturbed herbaceous pollen indicators represented. These levels indicate the continued utilisation of catchment resources through the Iron Age and Roman period into the Dark Ages. General features of the period include the continued expansion of acidic grassland dominated communities, and the persistence of Alnus and Corylus avellana albeit at reduced amounts.
The early Medieval period (MVLP4b) experiences further clearance in an environment that seems to be increasingly stressed. This activity is associated with a major increase in charcoal concentration at 65cm, and the almost complete removal of arboreal species, dated to AD 820-1035 (Table 6.1). Clearance is accompanied by an expansion of Filipendula, Potentilla, Lotus, members of the Rubiaceae family, Succisa pratensis and Cirsium species, all of which relate to damp acidic grassland communities (Rieley and Page, 1990; Hatton, 1991). It is likely that this clearance activity is linked to the mineral extraction processes operating in this area of the moor from as early as the 9th century AD (Greeves and Newman, 1996), since Alnus is well documented as a possible source of charcoal (McVean, 1953) for the early tanners (Simmons, 1962; Brown, 1977; Beckett, 1981; Caseldine and Maguire, 1981).

The clearance is tentatively related to a possible deterioration of climatic conditions and subsequent increase in blanket bog development, as reflected by the peaks for Sphagnum, Calluna and Cyperaceae at the MVLP4a/b boundary. It is possible that this expansion of blanket bog may relate to the increased levels of anthropogenic disturbance in the area, but also to a mid-first millennium AD climatic downturn (Blackford and Chambers, 1991). However, the validity of the climatic deterioration at this time remains largely unsubstantiated (Ballantyne, 1991) since the English temperature curve before AD 1100 is rather uncertain. However, recent investigations have suggested some indication of increased surface wetness of ombrotrophic mires from northern England around 1000 years ago (Barber et al., 1994).

Following this period a number of arboreal species appear in the pollen spectra, including Pinus sylvestris, Ulmus, Fagus sylvatica, Quercus, Betula, Alnus, Salix, Fraxinus and Corylus avellana, although it seems likely these would have formed a very patchy woodland. The largest proportion of this area consisted of acid grassland with associated herbaceous species characterised by Potentilla, Rubiaceae (probably Galium saxatile), Succisa pratensis, Plantago lanceolata and members of the Cyperaceae family (e.g. Carex and Eriophorum species).

The modern moorland: AD 1400 to present times

The upper two pollen zones characterise the late Medieval and more recent times indicating general stability in the area. However, grassland continues to increase in the area. The appearance of cereal type pollen grains in the upper sediments (45cm), dated to ca. AD 1400, relate to Medieval
agricultural practices, and characterise the most intensive tinning activity in the area, as indicated by
the concentration of industrial archaeological remains of this period. The presence of these grains
confirms arable practices were being carried out on the moor at this time, but it is likely that activity
was on a small scale, possibly resulting from activities at Shillapark Farm. The open moorland of
this time was utilised as common grazing land for sheep, with smaller amounts of cattle. A decline in
Calluna at the onset of MVLP6 may relate to more intensive use of the moorland in the form of
overgrazing, burning and afforestation around AD 1500 (Stevenson and Thompson, 1993). Again,
the presence of cereal type pollen indicates arable agriculture for the period after AD 1500. The
presence of Picea, Abies and Pinus sylvestris date the upper 10cms to around AD 1700 since the
first coniferous plantations were generally established after this date (Ratcliffe, 1984). Dartmoor at
this time was undergoing a change with respect to its land use. Enhanced technology had improved
the extractive efficiency of the tin ore smelting process meaning previously worked areas could be re-
worked to extract the small amounts of tin which were previously considered unproductive. The
moor saw the development of stone quarries, such as the nearby Merrivale and Fogintor quarries,
which would have provided materials for the implementation of infrastructure developments.

6.5 Discussion of the palaeoenvironmental development of the Upper Merrivale area
The basal sediments characterise a local fen carr community composed predominantly of Salix
species, with surrounding hill slopes dominated by Corylus-Quercus scrub woodland (Fig. 6.9,
Table 6.4). Open conditions are indicated by the presence of a number of taxa, including ferns,
Rumex species and Urtica dioica. Although it seems these openings may be natural components of
the woodland, since the indicators of physical erosion are low, with the other geochemical signals
suggesting stable conditions. The initiation of blanket bog development occurs at 125 cm (late
Mesolithic) as indicated by the increased abundance of Calluna vulgaris, Poaceae and Potentilla-
type pollen, in association with an increased presence of Alnus and charcoal fragments. This
evidence corroborates the suggestion presented by Moore (1988, 1993), but it is still not possible to
unequivocally state the dominant triggering mechanism for inception. However, in this location it
seems that the activities of the human population have been more than instrumental in the initiation
of pedogenic processes, inevitably resulting in large scale landscape degradation with subsequent
development of blanket peat. Continued deforestation is noted through the prehistoric period and into
the Roman and Dark Age periods. This substantiates further the claims made at Tor Royal that the
moorland resources were being actively utilised throughout these periods, despite scant

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<th>Geochemistry</th>
<th>Vegetation</th>
<th>Environment</th>
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<td>Coniferous plantations</td>
<td>Much grazing activity</td>
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<td>AD 820-1065</td>
<td>Dark Ages</td>
<td>Increasingly acidic conditions (loss of Fe, Al and bases)</td>
<td>Acidic grassland communities dominate</td>
<td>Area characterised by rough grazing pasture</td>
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<td>395-140 BC</td>
<td>Iron Age</td>
<td>Increased levels of Si, K, %ash</td>
<td>Falling Alnus, increasing Poaceae</td>
<td>Significant local disturbance activity</td>
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<td>395-140 BC</td>
<td>Bronze Age</td>
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<td>Inception of blanket bog</td>
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<td>Alnus rise</td>
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<td>6000 BC</td>
<td>Mesolithic</td>
<td>Stable elemental profiles (Na, K, Mg)</td>
<td>Corylus, Quercus, Betula, Salix plus ferns</td>
<td>Anthropogenic disturbance (charcoal)</td>
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<td>Mixed woodland with open patches</td>
</tr>
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Table 6.4 Summary of the palaeoenvironmental conditions at Upper Merrivale
Late Mesolithic/Neolithic

Local area dominated by damp woodland adjacent to the river, with hillside characterised by Corylus and Quercus. Increasing disturbance results in a pollen spectra composed increasingly of grasses and ruderal species. Blanket bog initiates around the same time.

Iron Age (400 BC)

A significant deforestation episode results in the recession of woodland conditions in the area and an expansion of grassland and blanket bog communities. Patchy hazel scrub is present on the hillslopes of this period, with alder still dominating the damp area around the River Walkham.

Dark Ages - Medieval - Present day

Open environment characterised by acidic grassland and blanket bog communities. Very infrequent tree species.

Figure 6.9 Schematic development of the Upper Merrivale area from late Mesolithic to modern times
archaeological evidence for settlement of these uplands areas. The indicators of physical disturbance increase and peak between 395-140 BC (100cm). Increases for Si, K and the mineral content (%ash) of the sediments in association with decreases for TOC and S indicate significant disturbance to the system in which mineral particles were deposited directly onto the mire surface. This episode is similarly reflected in the palynological data, and includes an increase in charcoal concentration, a reduced amount of arboreal species, particularly Corylus avellana, and an expansion of acidic grassland and blanket bog communities (Fig. 6.9). The nature of this evidence suggests a relatively large scale clearance of the local area using fire. This possibly relates to the final clearances of the late Bronze Age period, which opened the landscape sufficiently to allow increased run-off, with the transportation of mineral particles via water and wind borne vectors.

The post disturbance scene is one of stability, although the changed nature of the environment is reflected in the sediments of this period. Increased acidity is inferred from the low presence of a number of base elements and the expansion of blanket bog species. The period between AD 200-900 experiences a minor expansion of arboreal species and Corylus avellana, suggesting a recolonisation of small patches of woodland in the area. This also confirms the reduced levels of anthropogenic activity in the area (Quinnell, 1996). However, after ca. AD 1000 increased activity is again experienced. Declining levels of Alnus, and the other arboreal species in association with elevated levels of charcoal suggest active management of these local resources. This period indicates the start of tinworking in the River Walkham catchment, which continues for the next seven centuries. It is possible to suggest that the decreasing levels of Alnus in association with the elevated charcoal concentrations are directly attributable to the activities of the Medieval tinners, since this species has long been known to be suitable for the production of charcoal (McVean, 1953), an essential component in the early tin smelting process. However, the geochemical signals reveal no definite evidence for such activity. It was hoped the analysis would reveal elevated Sn contents at these levels, but given the problems outlined previously this may not be possible.

At ca. AD 1250 the first indications for arable crop production are obtained, possibly relating to activities around the nearby Shillapark Farm and the numerous stamping mills. The uppermost sediments indicate reduced levels of Calluna, as was observed at Tor Royal, and reflect the result of more recent mis-management of the moor in the form of overgrazing and uncontrolled burning. The presence of coniferous pollen above 25cm suggests a date of AD 1700 and indicates a more regional
pollen component produced from the plantations.

6.6 Discussion

Analysis of the sediments from Upper Merrivale has yielded much information about human interaction with the local landscape from late Mesolithic times. The geochemical data has provided important information to substantiate the palynological hypotheses presented, and identified a significant landscape disturbance episode dated to 395-140 BC in which deforestation appears to have resulted in the increased erosion of local catchment materials and an extension in acidic grassland and blanket bog communities. The more subtle changes to the catchment revealed by pollen analysis of the early historic and Medieval sediments are not replicated in the geochemical dataset, suggesting the geochemical signals to be dominated by autogenic processes during this period with a minimal input of allogenic material.

The limited use of a number of elements using EDMA was again illustrated. The heavy metals (Sn, As and Pb) were intercorrelated and thus of little use to the overall palaeoenvironmental interpretation, although elevated levels were detected in sediments from 100cm. Similarly the use of Mn and Mg is limited by the same problems. Again it is not clear whether these problems are inherently connected with the detection capabilities of the technique. Discussion of the remaining sites will hopefully further elucidate this factor.
Chapter 7

Piles Copse: investigation of an ‘ancient’ woodland and its environment

7.0 Introduction

This chapter presents the results from analyses conducted at Piles Copse on the River Erme, southern Dartmoor (Fig. 7.1). The site was chosen for the following reasons:

(i) the sampling sites lie in a similar situation to Upper Merrivale. There is much evidence for human activity in the area with a concentration of industrial archaeological remains associated with more recent tin working. The possibility existed to compare the palaeoenvironmental signals obtained from this site with those from Upper Merrivale, with emphasis placed upon the detection of prehistoric and historic tin working activities.

(ii) The site lies close to a suggested ‘relict’ woodland. A multi-core approach was adopted here to elucidate the antiquity of this ancient woodland and examine the geochemical signals for deforestation and other catchment activities.

(iii) The sampling of two cores from different sedimentary contexts but within 100m of one another provided the opportunity to examine whether regional palaeoenvironmental changes were detectable using different types of sedimentary material.

The first core (PC1) was extracted from a small spring fed hollow approximately three metres in diameter immediately adjacent to the northern tip of the woodland (Fig. 7.1; Plate 7.1). It was hoped this site would contain a significant local pollen component (Jacobson and Bradshaw, 1981; Prentice, 1985) and have a similar pollen catchment to that of a study conducted fourteen years previously (Roberts, 1983; Roberts and Gilbertson, 1994). PC1 most likely contained the greater proportion of its external mineral material from the River Erme, and as suspended material carried in overland flow from the adjacent slopes of Sharp Tor, immediately above Piles Corner. The second profile (PC2) was taken ca. 100m to the north of PC1 from an area of blanket peat on the gentle slopes above the River Erme (Plate 7.1), and as such provides a regional pollen signal since the site is situated in a more open location. The use of a multi-core approach allows the separation of different pollen components at varying spatial scales (Bradshaw, 1991; Edwards, 1991, 1983b), which is potentially useful in the investigation of the antiquity of the local Quercus woodland.
Figure 7.1 Location of Piles Copse, southern Dartmoor
CR83 illustrates the position of the coring site used in Roberts (1983)
Plate 7.1  Piles Copse. Sampling sites PC1 and PC2 are marked with arrows. The view is to the south west.
7.1 The status of the relict high level oak woodlands in the British Isles

There has been much discussion as to the origin and antiquity of the relict high level woodlands of the British Isles (Yapp, 1953; Archibald, 1966; Proctor et al., 1980; Rackham, 1986). These are suggested to be direct descendants of the mid-Holocene climatic climax woods, and would have experienced their maximum coverage of the British Isles around 4000 BC. The forests of these times were composed of *Quercus*, *Betula*, *Ulmus*, and *Corylus* with both a rich herbaceous and epiphytic flora. Activities of an increasing human population, climatic change and other factors saw the reduction of the majority of these woods, with only a few small pockets surviving in generally inhospitable areas confined mainly to the uplands of the British Isles. These existing remnants are characteristically small scale woods on steep river valley slopes. The trees frequently display a stunted growth form, an uneven age structure (Simmons, 1965) with a diverse and rich epiphytic flora (Harris, 1921; Tansley, 1939; Turner and Watt, 1939).

Three such woodlands exist on the Dartmoor upland: Wistman’s Wood, 3km north of Two Bridges (Harris, 1921; Anderson, 1953), Black Tor Copse on the West Okement river (Barkham, 1978), and Piles Copse (Roberts, 1983; Roberts and Gilbertson, 1994). The last is of particular interest and will be described briefly below.

Piles Copse is composed almost exclusively of *Quercus robur* (Harris, 1975). The slopes surrounding the woodland are largely open and dominated by *Pteridium aquilinimum* with abundant *Vaccinium myrtillus*, *Galium* species and members of the Cyperaceae family. However, small pockets of shrubby woodland exist and are composed largely of *Sorbus aucuparia* and *Salix* species, with *Crataegus monogyna* and *Sambucus nigra*.

Roberts (1983), however, questions the antiquity of this woodland, basing her conclusions on the even aged structure of the wood, an undated decline in *Quercus* pollen percentages and concentrations and the inferred activity of the 17th century during which time much wood was known to have been cut to produce charcoal for smelting practices. Others have also questioned the origin of the woodland (Christy and Worth, 1922: 325):

“...I feel certain, although I can produce no proof, that Piles Wood has been felled, in part at least. It is situate where the trees could be removed—not easily it is true! and probably it has been resorted to for timber and firewood, but this must have been very many years ago.”

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This investigation therefore seeks to extend the results of Roberts and further elucidate the origin of the modern woodland that exists today at Piles Copse.

7.2 Sampling regime

The area surrounding the woodland was probed to find suitable deposits for analysis. Two sites were selected as presented earlier. Samples were taken at 5cm intervals from each of the profiles. A finer interval was adopted in the upper section of the PC1 profile, between a depth of 15 and 30cm since in these samples the levels of arboreal pollen were subsequently found to be low, and therefore possibly related to a deforestation episode. Two samples were taken for AMS radiocarbon dating of the sediment, one from each profile at the levels where the arboreal pollen curve started to decline.

7.3 Radiocarbon dating of the Piles Copse profiles

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth (cm)</th>
<th>Lab-code</th>
<th>$^{14}$C age</th>
<th>Calibrated age (BP)</th>
<th>Calendar age (ref AD 1950)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>28-29</td>
<td>Beta-93820</td>
<td>540±50</td>
<td>640-500</td>
<td>AD 1310-1450</td>
</tr>
<tr>
<td>PC2</td>
<td>50-51</td>
<td>Beta-93821</td>
<td>240±60</td>
<td>440-0</td>
<td>AD 1510-1950</td>
</tr>
</tbody>
</table>

Table 7.1 Radiocarbon dates from Piles Copse

Calculation of accumulation rates using one date for each profiles is not possible, and normally a minimum of two, preferably three dates, are required. However, assuming the upper samples are modern the rate of accumulation between the dates and the top of the profile may be calculated. The upper 29cm of the PC1 profile therefore displays an accumulation rate of 0.056cm/yr$^{-1}$. Assuming the sediment accumulated at a reasonably constant rate up to 29cm, this gives the basal sample an extrapolated date of AD 300. This assumption is weak since it seems likely that the rate of accumulation has changed substantially, as reflected by the varying total pollen and spore concentration curve (Fig. 7.10).

Similar calculations using the data from PC2 are complicated by the wide age range of the date, although the mid-point of the calendar age may be used (AD 1730). It seems possible that the sediment developed at a more rapid rate than that of PC1, although more radiocarbon dates are required to confirm this suggestion.
7.4 Palaeoenvironmental reconstruction of the Piles Copse area

Discussion will be made of the profile stratigraphy followed by presentation of the geochemical results for each site, then the results from pollen analysis of each profile. Multi-variate techniques were used as presented in section 2.4, the results from which will be discussed in the relevant section.

7.4.1 Stratigraphical description

*Piles Copse core 1 - PC1*

The basal sediments are characterised by minerogenic matter with very few organic inclusions (Fig. 7.2). The material is most likely derived from weathered granite carried and deposited by the river during times of flood. There is a sharp transition at 74cm to a sandy organic deposit with infrequent, but identifiable organic remains. These mainly consist of decayed herbaceous rootlets with grass and sedge stems. The material overlying this unit becomes increasingly organic. Sediments between 52 and 60cm are characterised by a dark brown greasy deposit in which small mineral particles are visible, but vegetative remains are largely absent. The unit between 30 and 52cm is much the same as that of preceding levels but contains larger mineral particles up to 5mm in diameter, with more abundant macrofossil remains.

A significant change in sediment type is encountered between 27 and 29cm, which divides the upper and lower sediments. This unit is characterised by a layer of *Sphagnum* macrofossil remains into which the roots from the overlying unit penetrates. The material takes on a felted, heterogeneous nature with an absence of mineral material. The remaining sediments are essentially of this type, becoming lighter in colour and felted in structure. The uppermost unit is characterised by felted peat with abundant macrofossil remains, including *Sphagnum* mosses and woody fragments and roots.

*Piles Copse core 2 - PC2*

The lack of mineral matter is noted in the base of the profile (Fig. 7.3). The basal sediments are composed of brown felted organic material with abundant macrofossils, including *Calluna vulgaris* rootlets and stems. The main division of the sediment into stratigraphic units is possible only with reference to subtle changes in the nature of the sediment and the predominant macrofossil elements. The unit between 48 and 74cm is composed predominantly of *Sphagnum* remains, but is similar to the basal unit in both colour and structure. The sediment between 18 and 48cm is more humified than the preceding material and is considerably darker, but still displays abundant macrofossil components dominated by vegetative rootlets.
Light brown felted peat with abundant macrofossil remains. 

*nig* 2, *elas* 3, *sicc* 2, *humo* 1, *Tb* 2, *Tl* 1, *Dg* 1

Light brown felted unit with abundant rootlets.  

*nig* 2, *elas* 2/3, *sicc* 2, *humo* 2, *Th*(Sphagni) 3, *Dh* 1, *Dg* +

Dark brown greasy unit, well humified with mineral fragments visible.  


Very sandy deposit with few organic remains.  


Figure 7.2 Stratigraphy of Piles Copse sediment - core 1 (PC1)
Light brown felted peat dominated by *Sphagnum* macrofossils. 
nig.1 elas.4 sicc.0 humo.0 Tb(Sphagni)3 TII Th+ Dh+

Dark brown humified peat with abundant macrofossil remains. 
nig.3 elas.2 sicc.2 humo.3 Tbl Tl2 Th1 Dh+

Light brown felted peat dominated by *Sphagnum* remains, abundant monocot remains. 
nig.2 elas.0 sicc.1 humo.1 Tb3 TII Dh+ Dg+

Dark brown felted peat. Abundant macrofossils including *Calluna vulgaris* remains. 
nig.3/4 elas.2 sicc.1 humo.1 Tb1 TII Di2 Dg+ Ld+

Figure 7.3 Stratigraphy of Piles Copse sediment - core 2 (PC2)
The boundary of the uppermost unit is marked by a sharp transition. The sediments of these levels are once again dominated by well preserved *Sphagnum* remains, modern macrofossils and root material.

### 7.4.2 EDMA investigation of the Piles Copse sediment

Geochemical investigation of the two profiles from the Piles Copse area sought to address a number of different questions:

(i) the degree to which the signals from different sedimentary systems located close together were comparable;

(ii) whether both profiles detect the signals associated with the postulated mineral extraction and processing operations in the River Erme catchment, and;

(iii) the nature and scale of other anthropogenic activities in the surrounding area, including deforestation and possible afforestation practices.

The results from each profile will be presented individually. The results from PC1 are presented as elemental profiles (Fig. 7.4a,b) divided into four distinct chemizons which are described in Table 7.2. Multi-variate analysis of the geochemical data was undertaken and is presented in Figs. 7.5 and 7.6. The results from analysis of PC2 are similarly presented as elemental profiles (Fig. 7.7a,b), described in Table 7.3, with results from DCA in Figs. 7.8 and 7.9.

Initial observations of the results from both cores suggest the profiles of Mn and the heavy metal elements, Sn, As and Pb, to be of limited use when addressing the palaeoenvironmental processes operational in the Piles Copse area over the last 1500 years, although both Sn (PC1) and Pb (PC2) display elevated amounts in the basal material from each core, suggesting EDMA may be capable of detecting these elements when they contribute significantly to the overall geochemical signature of the sample. However, discussion will be focused upon the major elements, Si, Al, the mobile elements Fe, S and P, and the bases Na, K, Ca and Mg, since these seem to present the most reliable signals.

### 7.4.3 Multi-variate analysis of the Piles Copse EDMA data

*Piles Copse core 1 - PC1*

The elements on Fig. 7.5 seem to characterise a gradient of increasing mineral matter towards the right hand side of axis one, with elements more usually associated with organic material (TOC, P) present on the other end of the gradient. Axis two is more difficult to explain, but may relate to the pH status of the
Depth (cms below ground level)

Calendar years (2 sigma)

EDMA results from analysis of Flies Copse core 1 (PCI)

Figure 7.4a
A number of elements exhibit steady state equilibrium conditions in this zone: Al, P, S, Si, Na, K and Ca. The TOC curve increases gradually up through the zone from <5% at 90cm to c.25% at the boundary, while the %ash curve falls gradually over the same samples. Fe and Mg display fluctuating profiles but display generally declining trends through the zone.

Increases for S, P and TOC characterise this zone. %Ash falls through this zone from 55% at 50cm to 30% at 30cm. High levels of Si and Al are present.

Complex geochemical conditions are indicated in this zone by the erratic nature of the elemental profiles. Dynamic equilibrium conditions are demonstrated with a long-term declining trend for K, Fe, Al and Si. An increasing trend is exhibited for TOC and S. %Ash declines through PC1Gc to low levels at the upper zone boundary. The spiked nature of a number of profiles (Na, Ca, Cu and P) make interpretation difficult.

This zone indicates sediment containing high levels of TOC, a declining amount of Al, with fluctuations for a number of elements. The base elements, Na, K and Ca, experience increased amounts in this zone. Fe, Mg and Mn are present in very low amounts.

Table 7.2  EDMA results from analysis of PC1

<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1Ga</td>
<td>90-50</td>
<td>A number of elements exhibit steady state equilibrium conditions in this zone: Al, P, S, Si, Na, K and Ca. The TOC curve increases gradually up through the zone from &lt;5% at 90cm to c.25% at the boundary, while the %ash curve falls gradually over the same samples. Fe and Mg display fluctuating profiles but display generally declining trends through the zone.</td>
</tr>
<tr>
<td>PC1Gb</td>
<td>50-29</td>
<td>Increases for S, P and TOC characterise this zone. %Ash falls through this zone from 55% at 50cm to 30% at 30cm. High levels of Si and Al are present.</td>
</tr>
<tr>
<td>PC1Gc</td>
<td>29-15</td>
<td>Complex geochemical conditions are indicated in this zone by the erratic nature of the elemental profiles. Dynamic equilibrium conditions are demonstrated with a long-term declining trend for K, Fe, Al and Si. An increasing trend is exhibited for TOC and S. %Ash declines through PC1Gc to low levels at the upper zone boundary. The spiked nature of a number of profiles (Na, Ca, Cu and P) make interpretation difficult.</td>
</tr>
<tr>
<td>PC1Gd</td>
<td>15-0</td>
<td>This zone indicates sediment containing high levels of TOC, a declining amount of Al, with fluctuations for a number of elements. The base elements, Na, K and Ca, experience increased amounts in this zone. Fe, Mg and Mn are present in very low amounts.</td>
</tr>
</tbody>
</table>
Figure 7.5  DCA element plot of EDMA data from analysis of Piles Copse core 1 (PC1)
Cumulative percentage variance explained by two axes = 90.8%
Figure 7.7a.
EDMA results from analysis of Piles Copse core 2 (PC2).

Depth (cms below ground level)

Calendar years
(2 sigma)

%Na

%K

%Ca

%Mg

%Fe

%Mn

%S

%P

PC2a

PC3a

PC3Gc

Chemzones
TOC exhibits high stable equilibrium conditions with values of ca. 45%. A number of elements exhibit declining trends through the zone: Mg, Ca, Fe, S with only Si, Al, P and %Ash exhibiting increasing profiles.

The zone is dominated by Si and Al, the former of which increases through the profile with %Ash from 50cm to peaks at 20cm. Al remains static until the last three samples of the zone over which it declines. Fe increases from 50cm, with Mg disappearing at 45cm. S, Ca and TOC decline steadily over the zone.

This zone is dominated by Si which again shows a close association to %Ash. A number of elements increase through this zone: Fe, Ca, K, Cu and Al. The trace elements display inter-correlated profiles in this and all preceding zones.

<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC2Ga</td>
<td>83-60</td>
<td>TOC exhibits high stable equilibrium conditions with values of ca. 45%. A number of elements exhibit declining trends through the zone: Mg, Ca, Fe, S with only Si, Al, P and %Ash exhibiting increasing profiles.</td>
</tr>
<tr>
<td>PC2Gb</td>
<td>60-20</td>
<td>The zone is dominated by Si and Al, the former of which increases through the profile with %Ash from 50cm to peaks at 20cm. Al remains static until the last three samples of the zone over which it declines. Fe increases from 50cm, with Mg disappearing at 45cm. S, Ca and TOC decline steadily over the zone.</td>
</tr>
<tr>
<td>PC2Gc</td>
<td>20-0</td>
<td>This zone is dominated by Si which again shows a close association to %Ash. A number of elements increase through this zone: Fe, Ca, K, Cu and Al. The trace elements display inter-correlated profiles in this and all preceding zones.</td>
</tr>
</tbody>
</table>

Table 7.3       EDMA results from analysis of PC2
Figure 7.8  DCA element plot of EDMA data from analysis of Piles Copse core 2 (PC2)

Cumulative percentage variance explained by two axes = 64.8%
Cumulative percentage variance explained by two axes = 64.8%

Figure 7.9 DCA sample plot of EDMA data from analysis of Piles Copse core 2 (PC2)
developing system.

There are two clear associations on the sample plot (Fig. 7.6). Group one includes samples between 29 and 90cm and group two which includes all the remaining samples. It seems that the postulated disturbance activity which initiates at 29cm forms the basis for the boundary, with the geochemical signals above this level displaying significantly different characteristics to those below.

**Piles Copse core 2 - PC2**

Again it seems feasible to explain axis one in terms of the mineral-organic material continuum, with those elements usually associated with clastic matter present towards the left of the plot. Axis two presents a confusing picture, which cannot simply be explained in terms of clearly discernible environmental gradients. It therefore perhaps relates to a combination of factors.

Multi-variate analysis of the samples from PC2 produced a plot in which the samples were arranged generally from right to left, suggesting long term geochemical trends are more important than single events, as confirmed by the increasing trends for Si, Fe, K and %ash, with a sustained decrease for Ca, S, Mg and TOC. Axis one on Fig. 7.9 therefore serves as a time scale with oldest samples on the right of the plot.

### 7.4.4 Interpretation of the geochemical signals from Piles Copse

**Piles Copse core 1 - PC1**

**The basal samples - initial status of the system**

The indicators of physical erosion, Na and K, together with Si and Al are stable. This combination of elements most likely relates to the composition of the mineral material dominating the basal section of the core. Ash values, taken as a first approximation of the concentration of mineral matter (Aaby, 1986; Shotyk, 1996b), reach values up to 90% in PC1Ga confirming the minerogenic nature of the sediment at this time. It seems likely that this material was deposited directly by the River Erme during times of flood. The alumino-silicate associations and base element signatures of this sediment are derived from the locally weathered granite (Brunsden and Gerrard, 1977). The stable elemental profiles relate to the constant input of this material into the sedimentary system. The presence of P, TOC and S suggests the steadily increasing status of the organic matter from 90cm.

The Fe signal possibly suggests the sedimentary system was under oxidised conditions in the basal
section of the core, but the widely fluctuating nature of this profile in this basal zone may relate to pulses of mineral material, since the element may have been transported to the sedimentary system in particulate form as inorganic oxides, or oxide coatings on mineral material (Jones and Bowser, 1978). It seems that this activity may have subsequently led to anaerobic conditions as the peat system develops. This progression to more anoxic, waterlogged conditions are confirmed by the increasing S content since this element likely relates to the formation of H₂S and metal complexes under reducing conditions (Gill, 1989). It appears that these conditions are experienced to modern times due to the absence of Fe, particularly in the upper levels confirming a predominantly anaerobic sedimentary environment, in which sulphide production becomes increasingly important.

The elevated base status of the system in PC1Ga may have been maintained by the introduction of semi-weathered granitic mineral material, as suggested earlier. This material has an elevated Sn content which serves to illustrate no more than the local rocks are enriched in this element.

The next zone (PC1Gb) seems to indicate an environment becoming increasingly anoxic. Lower Fe values and increasing S suggests the sedimentary environment is dominated by anaerobic, acidic conditions (Goldschmidt, 1954; Mackereth, 1965, 1966; Engstrom and Wright, 1984; Naucke et al., 1993).

A peak for K and %ash in association with a reduced TOC content at 45cm may relate to the introduction of mineral material. However, K is then seen to decline quite rapidly, possibly indicating a short lived physical disturbance phase. Increases for TOC, P and S after this episode relate to the continued development of the peatland system, in which Na, Ca, Mg and Mn are mobilised as the peat becomes increasingly anaerobic and acidic. The gradual decline of ash in PC1a and b relates to the increased input of mineral matter as the sediment accumulates beyond the level of the river influence, except in times of high flow.

An environmental change

The boundary between PC1Gb and c is marked by a dramatic change in a number of elemental profiles (Fig. 7.4a/b). This change occurs as a boundary threshold between earlier lower values and later higher ones for Al, S, P and TOC, with a decline to levels for K, Si and %ash. The nature of
this change seems to relate to a decline in the introduction of clastic elements, and an increase in organic sedimentation as confirmed by the presence of those elements characteristic of autogenic peatland processes. The boundary between these two chemization zones marks the suggested onset of deforestation in the locality detected in the pollen record (section 7.4.6). These sediments do not exactly agree with this hypothesis since increased deforestation activity may result in an increased introduction of mineral material. This suggests the possible deforestation episode was not occurring immediately upslope from PC1. It appears that the sediments of PC1Gc become more acidic since Fe and K are lost and S increases. The association between S and Cu relates possibly to the formation of copper sulphides in the now anaerobic sedimentary environment. The increased acidity of this zone may relate to a number of separate inter-related factors including increased run-off generation through reduced woodland cover in the locality, with the subsequent effect of lowering pH which increased the mobilisation of K, Fe and Al (Williams et al., 1984, 1986; Muscutt et al., 1993). A change in the local vegetation may also trigger certain changes in the peatland system, e.g. Calluna vulgaris is capable of producing locally increased environmental acidity through the liberation of polyuronic acids (Grime et al., 1988; Rieley and Page, 1990). These suggestions will be discussed with reference to the pollen data.

The upper sediments of PC1 (PC1Gd) are dominated by complex bio-chemical processes operational within the acrotelm of the system. These include bio-accumulation of K in the surficial sediment (Shotyk, 1988), and the peak of Cu and S, due most likely to the formation of sulphides at the Eh boundary. Absence of Fe in the upper sediments is explained by the likely anoxic surficial sedimentary environment, confirmed by permanently waterlogged conditions.

Piles Copse core 2 - PC2

The indicators of physical erosion, Na, K, Mg, Ca, and Si are present in small amounts in the basal zone (PC2Ga). However, some may relate to autogenic processes. For example, Ca has a strong affinity with organic ligands (humic and fulvic acids), as such a body of sediment may contain much Ca not associated with allogenesis (Engstrom and Wright, 1984). This element may thus have limited use as a palaeoenvironmental erosion indicator. Similarly the gradual decline for Mg may relate to post-depositional mobilisation of the element, since it is has a weak adsorption potential to decomposing organic matter, and thus forms unstable organic complexes which are readily leached from the peatland system, especially if the pH of the circulating water is low (Shotyk, 1988).
Mg signal may simply illustrate the system was becoming progressively acidified during this phase of accumulation. The low levels of %ash in the basal zone suggest minimal input of clastic materials at this time.

A high S content of the peat most likely relates to the presence of sulphides in the anaerobic zone. The relationship to TOC therefore indicates the status of organic matter in the sedimentary system. It seems probable that the peatland environment is anoxic by the time represented by the upper sediments of this zone, due to the absence of Fe which is readily mobilised under anaerobic and low pH conditions (Goldschmidt, 1954). The lack of correspondence between the Si and Al profiles suggests that neither element relates primarily to the presence of alumino-silicate mineral associations, other processes being more important, in which the availability of organic C influences the presence of Al.

The heavy metal elements appear difficult to interpret. As and Sn display very similar profiles in this zone, which may be a result of the procedures inherent to the EDMA technique. However, elevated levels of Pb are detected in the basal zone, confirming the material at this time to be relatively enriched in this element. Again this strengthens previous suggestions of the general inefficiency of EDMA for the analysis of trace and heavy metal elements from most peatland systems.

The next zone (PC2Gb) exhibits indications for oxidised conditions in the sediment body (e.g. Fe), with a possible rise in pH, which may explain the slight increase in Al to 30cm. Similarly K demonstrates increased values from 40cm indicating a possible rise in pH levels. Further corroboration for this suggestion is provided by the increased Fe content of sediment above 50cm. A number of elements which may be linked to organic matter and associated biological processes are shown to decline: S, TOC and Ca indicating a degradation of catchment materials through time. TOC in particular illustrates a long term declining trend which may relate to the natural sequence of progression for such a sedimentary system, given the changing nature of activity in the local environment.

In the upper sections of PCGb (ca. 30cm) the system displays continued indications for disturbed, oxidised conditions: increased Fe with declines for Mg and Ca possibly relating to increased pore-water acidity. The primary indicator for increasing disturbance is the increased ash content of the
sediment, which is comparable to the Si profile, indicating the material to be derived from local catchment rocks. The introduction of this mineral matter may relate to increased catchment disturbance resulting from deforestation or mineral extraction and processing operations. The specific nature of the disturbance may become apparent in the discussion of the pollen analysis data. The oxygenated nature of the sediments provide suitable conditions for a set of complex biochemical processes to become operational, in which aerobic microbial activity will increasingly play a role, resulting in the increased humification of sediment between 18 and 48cm (Fig. 7.3).

The system is shown to exhibit increasingly oxidised conditions into $PC2Gc$. Fe increases, while S and TOC fall, possibly a function of microbial decomposition under oxygenated conditions. The zone is marked by increases for the indicators of erosion, Ca, Na and K which would relate to small scale/low intensity activity since there is little effect on the long term trend for TOC. The uppermost sediments display processes operational within the acrotelm. Similar conditions are noted as existed in $PC1Gd$ including bio-accumulation of K, precipitation of organo-metal complexes and sulphides at the acrotelm-catotelm boundary at ca. 5cm.

Summary of the geochemical history of the Piles Copse area

The basal levels of both cores indicate the presence of mineral matter, and the increasing status of the organic sediment. $PC1$ initially displays oxidised conditions, whilst $PC2$ indicates a more anaerobic situation in the basal levels of the profile which may similarly be neutral given the levels of Ca between 65 and 83cm. At $PC1$ the next phase of sediment accumulation is dominated by increasingly anaerobic conditions in which sulphides may have formed. $PC2$ however indicates increasingly oxidised conditions, with a gradually increasing base status and/or the introduction of mineral material elevated in Ca, Na and K in the uppermost sediments. A minor erosion episode is inferred from the signals of $PC1$ at 45cm in which %ash and K content is elevated, matched by a reduction in TOC. From this level upwards the sediment seems to display the indications of becoming increasingly anaerobic and acidic, although there are no further increases for the indicators of external environmental disturbance.

It seems that comparison of the individual elements is generally not possible between profiles. A number of factors may explain this including differing rates of accumulation, varying sample selection strategies and intervals, variations within the peat accumulating system through time, and the general sensitivity of each system with respect to retention and mobility of different elements. Both sites failed to produce convincing
geochemical evidence for the exploitation of local mineral resources, which may relate as much to problems of the analytical technique as to the retention/mobility of these elements in peatland sediments, although elevated levels of Sn and Pb were detected in the basal sections of each core. PC1 displayed increasingly acidic conditions from the level of postulated deforestation activity, but did not exhibit the expected increased levels of mineral matter, suggesting the activity occurred some distance from the coring location. No such activity was detected in the sediments from PC2.

7.4.5 Pollen analysis of the Piles Copse sediment

The palynological investigation of the sediments was aimed at investigating the antiquity and status of Piles Copse, an area of suggested relict ancient woodland on the upper reaches of the River Erme. The site would also provide indications for the disturbance created by tinning and associated activities in the area, and as such act as a comparison to the Upper Merrivale site.

Initial observations of the data from both profiles suggest some deforestation activity to have occurred in the locality in the more recent sediments, primarily focused upon the *Quercus* woodland. Discussion will be directed to the implications of this activity as well as the general pattern of vegetation change in the catchment as a whole. The results are presented as percentage pollen diagrams (Figs. 7.10 and 7.11) and described in Tables 7.4 and 7.5. The data are shown as percentages of Total Land Pollen (TLP). The DCA plots from the data analysis are presented as follows: core one species plot, Fig. 7.12; sample plot, Fig. 7.13; core two species plot 7.14; sample plot, Fig. 7.15, and are described below.

7.4.6 Multi-variate analysis of the Piles Copse pollen data

*Piles Copse core 1 - PC1*

Investigation of the species data using DCA techniques reveal a number of discrete assemblages. The first group (α) relates to species indicative of the local *Quercus* dominated woodland in which various fern taxa are represented. This may indicate the present day status of the vegetation of Piles Copse (Harris, 1975; Roberts, 1983). Group β includes a large number of species dominated by scrub and damp woodland components including *Corylus avellana*, *Calluna vulgaris* with *Alnus*, *Cyperaceae* and *Filipendula*. This group may belong to the pre-deforestation activity period. Assemblage γ includes species primarily associated with disturbed habitats, and seems likely to relate directly to the deforestation activity between 15 and 30 cm. The last group (δ) include taxa associated with damp habitats, including *Sphagnum* and *Salix* species. These plants serve to indicate the general status of the wetland flora in the area.
Table 7.4 Description of Piles Copse core 1 (PC1) local pollen assemblage zones

<table>
<thead>
<tr>
<th>LPAZ</th>
<th>Depth (cm)</th>
<th>Description of pollen zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1a</td>
<td>90-57</td>
<td>Poaceae, Corylus avellana, Calluna vulgaris, Quercus</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low Quercus, low stable AP. Corylus declining gradually to ca. 10% at PC1b. Poaceae increases gradually over same period. Abundant herbs and spores types.</td>
</tr>
<tr>
<td>PC1b</td>
<td>57-29.5</td>
<td>Poaceae, Corylus avellana, Quercus, Calluna vulgaris</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quercus seems more stable. Low Corylus, and Calluna stable through zone. Poaceae and herbaceous flora peak at start of zone.</td>
</tr>
<tr>
<td>PC1c</td>
<td>29.5-14</td>
<td>Poaceae, Potentilla, Cyperaceae, Quercus</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AP minimal, generally all trees represented as traces. Poaceae dominates pollen spectra, with an increase in certain herb taxa, e.g. Potentilla and members of the Cyperaceae family. Appearance of Pinus sylvestris and Picea in this zone. Low spore counts through PC1c.</td>
</tr>
<tr>
<td>PC1d</td>
<td>14-0</td>
<td>Poaceae, Cyperaceae, Calluna vulgaris, Quercus, Potentilla</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Increasing AP, dominated by Quercus, Betula and Pinus. Increasing heathland components in this zone. Stable herbaceous taxa dominated by Poaceae, with a recovery of spore types.</td>
</tr>
</tbody>
</table>

Table 7.4 Description of Piles Copse core 1 (PC1) local pollen assemblage zones
Cumulative percentage variance explained by two axes = 64.6%

Figure 7.12 DCA species plot of pollen data from analysis of Piles Copse core 1 (PC1) sediment (Species shown all have occurrences >1% TLP in >5 samples)
Cumulative percentage variance explained by two axes = 64.6%

Figure 7.13  DCA sample plot of pollen data from analysis of Piles Copse core 1 (PC1) sediment
Figure 7.11

Piles Copse core 2 (PC2) percentage pollen diagram
Exaggeration factor x10; + indicates a trace occurrence (<1% TLP)

Calendar year (2 sigma)

Figure 7.11

Piles Copse core 2 (PC2) percentage pollen diagram
Exaggeration factor x10; + indicates a trace occurrence (<1% TLP)
### Description of pollen zone

<table>
<thead>
<tr>
<th>LPAZ</th>
<th>Depth (cm)</th>
<th>Description of pollen zone</th>
</tr>
</thead>
</table>
| **PC2a** | 83-57 | Poaceae, Cyperaceae, Potentilla-type, *Pteridium aquilinum, Quercus*  
AP ≤5%, stable and dominated by *Quercus*. Spectra characterised by Poaceae (≥50%) and Cyperaceae. Herbaceous taxa include *Plantago lanceolata, Rumex* species, Potentilla-type and members of the Rubiaceae family. Pteridophyte species are dominated by *Pteridium aquilinum*. |
| **PC2b** | 57-22 | Poaceae, Cyperaceae, Potentilla-type, *Calluna vulgaris*  
AP largely disappears. *Pinus* increases from 35cm. *Calluna vulgaris* increases to a peak at 35cm (15%). Herbaceous taxa are again dominated by Poaceae and Cyperaceae, the latter experiencing a peak at 35cm. Other species include Potentilla-type, Rumex, *Hydrocotyle vulgaris* and members of the Rubiaceae family. |
| **PC2c** | 22-0 | Poaceae, Cyperaceae, *Pteridium aquilinum, Quercus*  
AP increases gradually through zone, dominated by *Quercus, Betula* and *Pinus sylvestris*. Herbaceous species are characterised by Poaceae which declines gradually through the zone and Cyperaceae which fluctuates through the upper samples. Potentilla is replaced in the uppermost samples by *Rumex, Lotus* and members of the Rubiaceae family. *Pteridium aquilinum* becomes a significant component of the vegetation towards the top of the profile. |

Table 7.5 Description of Piles Copse core 2 (PC2) local pollen assemblage zones
Figure 7.14 DCA species plot of pollen data from analysis of Piles Copse core 2 (PC2) sediment (Species shown all have occurrences >1% TLP in >5 samples)
Figure 7.15  DCA sample plot of pollen data from analysis of Piles Copse core 2 (PC2) sediment

Cumulative percentage variance explained by two axes = 48.0%
The sample plot produced three clearly distinguishable groupings. Group I includes samples between 65 and 90 cm and illustrates the initial state of the vegetation. This group relates to groups α and β of Fig. 7.12 and seems to indicate Corylus and Poaceae dominated habitats. The second sample assemblage is group II which includes samples between 30 and 60 cm. These samples are indicative of the more stable conditions which immediately predate the next group. The last group (III) include those samples from 30 cm to the surface, and include the levels in which the inferred deforestation activity is found.

_Piles Copse core 2 - PC2_

The species data from PC2 (Fig. 7.14) do not form as clearly defined groups as the data from PC1. However, group ε includes those species associated with the woodland in the locality, with Quercus, Corylus, Alnus, Betula, Fagus and Fraxinus represented. Group ϕ includes those species characteristic of more disturbed, acidic grassland habitats, possibly indicating the status of the local grassland communities throughout the time of sediment accumulation. The last assemblage group (γ) includes species more typically associated with damp acidic habitats. It is interesting to note that no group clearly identifies the deforestation activity noted in the discussion of PC1. The sample plot (Fig. 7.15) produced two groups: IV and V. It does not seem possible to clearly identify the causative factors for association since group IV included the majority of samples, and group V with the remainder, possibly relating to outliers in the data set.

7.4.7 Interpretation of the Piles Copse pollen data

_Piles Copse core 1 - PC1_

_The initial status of the vegetation_

The basal zone reflects a grassland dominated environment with local patches of heath vegetation and Corylus scrub. Quercus, Betula and Alnus were present in the sparse woodlands of the area. The gradual decline in Corylus does not appear to have been a function of increased shading, since the AP/NAP ratios indicate largely open conditions. This suggests selective clearance of the shrub. The heathland is composed of Calluna vulgaris, with only a sparse occurrence of Vaccinium-type pollen (including such species as Erica and Vaccinium), and herbaceous taxa including Potentilla, Scabiosa and members of the Rubiaceae family. It is likely that the ericaceous species were present in the immediate locality given the poor dispersal capabilities of this group of plants (Evans and Moore, 1985). The grassland component is indicative of a disturbed acidic community with species including members of the Lactuceae, Chenopodiaceae and Caryophyllaceae families, Rumex species and Plantago lanceolata.
(Ward et al., 1972; Rieley and Page, 1990). High levels of charcoal in the basal zone suggest landscape disturbance, although the lack of significant disturbance horizons in the spectra from PC1a indicate a more regional source for this activity.

The next zone (PC1b) characterises an environment dominated by grassy-heathland communities. An indication for increased wetness at the extra-local scale is provided by the appearance of *Menyanthes trifoliata* and the reappearance of *Hydrocotyle vulgaris*, both species favouring unshaded mires extending to areas adjacent to water (Grime et al., 1988). This zone experiences a minor expansion of herbaceous taxa with a subsequent increase in floristic diversity. Species such as *Urtica, Lotus, Jasione montana*-type and *Valeriana officinalis* are represented in the spectra confirming disturbed grassland habitats. The woodland component of the environment appears relatively stable, contributing ca. 10% of TLP. The presence of *Hedera* possibly suggests increased shading in the woodland areas, since the shrub can tolerate diminished light intensities (Stace, 1991), with *Polypodium* most likely an epiphytic component of the oak woodland (Turner and Watt, 1939; Roberts, 1983). The appearance of cereal-type pollen grains in this zone may relate to Medieval arable cultivation activities in the area, although dating of the sediment is problematic. Assuming a Medieval date for these grains indicates a similar episode of activity to that experienced in other parts of the moor at this time, and suggests a change in land use, away from the pastoral episodes of prehistory and early historic times (Tor Royal, Chapter 5; Upper Merrivale, Chapter 6; Shaugh Moor, Beckett 1981; Holme Moor, Maguire et al., 1983).

*Increased activity: disturbance of the oak woodlands*

The spectra of PC1c show a disturbance phase in which the local *Quercus* woodland seems to disappear, or is so severely affected that flowering capabilities are reduced for a substantial period of time. This is associated with an increase for Poaceae, *Potentilla* and Cyperaceae. The disturbance recorded in this zone seems to take place over three separate stages, corresponding to three peaks of the charcoal curve at 16, 23 and 29 cm depth. It seems that each individual stage accelerates the change to acidic grassland conditions in the catchment, since AP falls progressively, while Poaceae expands.

Falling levels of pteridophyte species, associated with reducing arboreal pollen values and the increased levels of charcoal, suggest these plants were primarily a component of the woodland and generally not part of the open moorland communities at this time. It seems that the activity recorded in these sediments indicates the area surrounding Piles Copse, and indeed the woodland itself may have been completely
cleared, since AP falls to its lowest values yet experienced (≤2% TLP) and probably represents a more regional component of the spectra since it includes Ulmus and Fagus. Both of these species are more likely to have been elements of the vegetation in the lower lying areas, and on the fringes of the moor. This activity may have been contemporary with the later phases of tinning activity on Dartmoor, since the radiocarbon evidence suggest the onset of this disturbance to have occurred between AD 1310-1450. It has been previously suggested that falling Alnus, and possibly Quercus values, may relate to deforestation to provide wood for charcoal (Simmons, 1964a; Brown, 1977; Beckett, 1981). Both species are seen to diminish rapidly following the first peak of microscopic charcoal in PCIc dated to ca. AD 1400.

The possibility of the modern woodland at Piles Copse being planted during the tinning episode exists. Roberts (1983) suggests the woodland may have originated in this period. Previous analysis of the woodland confirmed the floristic uniformity and even aged structure of the woodland (Harris, 1975). Extrapolation of the radiocarbon date suggests the Quercus curve recovers after AD 1700 (15cm), which may be considered as the last major phase of tinning activity on Dartmoor (Gerrard, 1996). It may be the case that the wall around the woodland (Fig. 7.1) was constructed to prevent grazing of the new saplings. A plantation would explain the even age structure of the trees, also the fact that the trees are almost exclusively Q. robur. It would similarly explain the low Quercus values for this pollen zone since the trees would be trying to become established in a degraded environment, and as such would exhibit a reduced flowering efficiency with subsequent diminished pollen productivity. However, other species also recover during this time (e.g. Betula and Pinus sylvestris) suggesting general recovery of arboreal species was occurring, perhaps in a location more remote from the sampling site, in which Quercus could well have been a component.

**The post-disturbance environment**

The uppermost zone of PCI relates to increasing stability. Arboreal pollen increases to its maximum for the profile (20% TLP) and is dominated by Quercus, with smaller amounts of Betula, Alnus, Pinus and Fraxinus. Calluna vulgaris is represented following the disturbance of the preceding zone. The herbaceous taxa are dominated by grasses, with other species such as *Potentilla*, members of the Cyperaceae, Rubiaceae and Rosaceae families. The lowered Poaceae percentages of PCIId most likely relate to the shading provided by the developing local woodland. However, the still significant amount of Poaceae pollen associated with persistent representation of *Potentilla, Plantago lanceolata* and *Pteridium aquilinum* with other herbaceous and Pteridophyte taxa suggest the continued presence of large tracts of
Piles Copse core 2 - PC2

Basal conditions

The basal zone indicates a predominantly open environment characterised by disturbed grassland communities composed of grasses and sedges, *Potentilla*, *Rumex* species and members of the Rubiaceae family. Low levels of charcoal indicate low intensity fire activity, possibly with a regional source. *Quercus* dominates the arboreal pollen spectra, but is represented at less than 3% TLP, suggesting either a low presence of this species, or the species was present further from the sampling site. It seems likely that there was only a very sparse woodland component at this time. The presence of small patches of scrub are indicated by *Corylus avellana*-type pollen, and areas of heath vegetation indicated by the presence of heathland allies including *Calluna vulgaris*.

It is difficult to directly establish the evidence for anthropogenic activity in this zone since the spectra indicates a severely disturbed environment, which may relate to previous periods of activity.

Increasing anthropogenic disturbance - demise of the Quercus woodland

The indications for disturbance activity increase into the next zone (PC2b) with falling AP; *Quercus* disappears completely at 35cm. A possible change in the hydrological condition of the peatland system is suggested by the increased occurrence of *Hydrocotyle vulgaris* and *Sphagnum* species in the bottom of the zone. Both species are able to tolerate high water tables. This may relate to increased runoff through such processes as woodland management, or increased river flow which may enhance the possibility of regular flooding in these areas marginal to the river course. The sedges similarly increase to 35cm which may relate to increased local wetness. Grass pollen remains relatively stable through the zone as does *Potentilla*-type and *Plantago lanceolata*. *Potentilla* supports the notion of increasing acidity and openness (Caseldine and Hatton, 1993), while *Plantago lanceolata* is "chiefly associated with poor, exhausted soils" (Grime et al., 1988: 438).

The disappearance of *Quercus* pollen at 35cm suggests complete removal of oak trees in the area, including the suggested ‘ancient’ woodland of Piles Copse. This is tentatively confirmed by the total absence of the spores of *Polypodium*, which would have been an epiphytic component of the oak woodland, as suggested for PC1. It seems the appearance of species which tolerate waterlogging in
this zone may indicate regular flooding in the low lying areas downslope. The pollen spectra around 35cm are probably contemporary with the disturbance episode recorded in PCIc, although interpretation of the radiocarbon evidence from PC2 is hindered by the wide age range of the calibrated date (Table 7.1). It seems possible that the data from both cores are comparable and the activity relates to a period of ca. 300 years from AD 1400 to 1700.

The post-clearance environment

The next pollen zone (PC2c) is marked by falling grassland pollen percentages and expanding Pteridium values. The uppermost samples indicate increasingly disturbed conditions, with Rumex acetosa, R. acetosella, Lotus, Rubiaceae, Sinapis-type, and members of the Asteraceae family represented. The pollen evidence indicates an area which becomes increasingly stressed as time progresses. The re-appearance of Quercus pollen at 25cm is significant since this must either relate to pollen produced by trees in the local area i.e. due to plantation, or from a more distant source as discussed for PC1.

7.5 Discussion of the palaeoenvironmental development of the Piles Copse area

The basal levels of both cores indicate an environment characterised by extensive areas of acidic grassland communities, with smaller heath and woodland components (Table 7.6). Disturbance in these sediments is indicated by the introduction of mineral material which displays elevated base elements contents and most likely derives from the partially weathered local granitic material. The results from PC1 suggest this material to be derived mainly from the River Erme, which plays a diminishing role as the sediment accumulates above the level of seasonal river flow. Whilst at PC2 the mineral material seems mainly a component of hill-wash, with the possibility of flood derived material during periods of high river flow.

Woodland in the area appears sparse and contributes less than 10% TLP. It is composed of Quercus with smaller amounts of Betula and Alnus. The presence of considerable amounts of charcoal in the basal levels of both profiles suggests anthropogenic activity, but the lack of palynological indicators for disturbance suggests the clearance and utilisation of fire to be on a more regional scale. The identification of cereal pollen between 35 and 45cm in PCI places this activity to be occurring after AD 1200 (Allan, 1996; Henderson and Weddell, 1996).

The systems are geochemically dissimilar with the basal levels of each profile indicating different
<table>
<thead>
<tr>
<th>Time</th>
<th>Geochemistry</th>
<th>Vegetation</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>Acrotelm processes.</td>
<td>Acidic grassland dominates</td>
<td>Pastoral land use</td>
</tr>
<tr>
<td></td>
<td>Anaerobic PC1; aerobic PC2</td>
<td>Piles Copse (<em>Quercus robur</em>)</td>
<td>Afforestation of Piles Copse</td>
</tr>
<tr>
<td></td>
<td>Increasing mineral matter (PC2, 20cm)</td>
<td>Increasingly open acidic</td>
<td>Tinning activity inferred from archaeological evidence</td>
</tr>
<tr>
<td></td>
<td></td>
<td>grassland with associated herbaceous flora</td>
<td>Deforestation of local woodland resources, charcoal</td>
</tr>
<tr>
<td>AD 1700</td>
<td>Increasing acidity, environmental threshold exceeded PC1</td>
<td>Local cereal cultivation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygenated sedimentary environment PC2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AD 1400</td>
<td>Low input of mineral matter PC1, PC2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AD 1200</td>
<td>Deposition of mineral matter from River Erme (PC1); oxidised sedimentary</td>
<td>Area dominated by grass and</td>
<td>Low scale deforestation activity, possibly regional.</td>
</tr>
<tr>
<td></td>
<td>environment (Fe), high base status (Na, K)</td>
<td>heathland communities. Sparse</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mixed woodland</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.6 Summary of the development of the area around Piles Copse
environmental conditions. PC1 is dominated initially by oxidised conditions which become progressively anaerobic as organic sedimentation initiates resulting possibly in the production of metal sulphide complexes and the loss of a number of base elements. PC2 seems to be characterised by anaerobic conditions from the basal sample. Increasing disturbance is encountered in both cores from mid profile levels upwards. At 45 cm in PC1 the signals indicate physical disturbance in the vicinity in which mineral material was deposited directly on the accumulating mire surface, itself reducing the level of TOC and possibly the productivity and status of the mire for a period of time. The sediments from PC2 similarly indicate increasing disturbance, but of a more sustained nature. Mineral material is incorporated into the sediment from 60 cm upwards, and seems associated with increased levels of acidity. The nature of this disturbance seems linked to the activities in the catchment at this time, although the indicators of physical erosion are not present in PC1 between 15 and 30 cm (ca. AD 1400-1700). The increased acidity of the system may relate to the operations in the catchment as a whole. During this time it seems likely that the *Quercus* dominated woodlands of the locality were severely reduced in extent. The use of two profiles has confirmed that the *Quercus* pollen in the profiles was due primarily to local woodland, similarly it seems that the signal presented in LPAZs PC1c and PC2b are contemporary and indicate a significant deforestation episode which took place over a number of discrete phases, possibly three as suggested by the charcoal curve from PC1. The step like nature of activity seems to have placed increasing levels of stress upon the developing peatland at this time resulting in a gradual but definite progression to more acidic, anaerobic conditions after AD 1700.

The geochemical differences between PC1 and PC2 for samples associated with this deforestation activity may be explained by the different types of sedimentary system, and the relative location of each site from the activity. It appears that it is not possible to directly compare the signals obtained from the differing peat forming systems due to a number of factors, including relative distance from activity, the nature of the active autogenic and subsequent post-depositional processes.

The increased levels of *Quercus* pollen after these times suggest the plantation of Piles Copse occurred after ca. AD 1700, and was thus possibly linked to the later phases of tin working in the Erme valley. The suggestion of Piles Copse resulting from an 18th century plantation explains the even aged structure of the woodland and also mono-culture nature of the woodland species.

The next chapter examines the development of a lowland mire in Cornwall, in which there is significant
evidence for anthropogenic disturbance focused primarily upon mineral processing operations. This site therefore seeks to investigate the geochemical record associated with this activity as a test of the efficacy of EDMA in a different sedimentary environment.
Chapter 8
Investigation of a lowland Cornish site: Crift Down

8.0 Introduction

This chapter presents the results from analyses carried out at a lowland site in Cornwall. Whilst there are now informative data from the uplands of Bodmin Moor (Conolly et al., 1950; Brown, 1977; Gearey, 1996; Gearey and Charman, 1996), there are almost no data from the lowlands. However, the nature of landscape change in this area is important in addressing questions concerning the division between upland and lowlands in the prehistoric and later periods. Analysis of these sediments is therefore of considerable importance in addressing a number of different factors in this project:

(i) the site is located at a lower altitude and is characterised by metamorphic slate lithologies, although granitic rocks of the St. Austell formation are found in the vicinity at nearby Helman Tor. Therefore, the sampling site may display a different set of sedimentary conditions, since it is not directly associated with the acidic granitic rocks of the peninsula. The site may have had a higher pH status, with a greater concentration of base elements.

(ii) Crift Down forms part of a significant Medieval tin extraction and processing area, with abundant field evidence including overturned river gravels, mounds of slag material and processing installations. Archaeological excavation of a nearby industrial complex has confirmed the importance of the site, and suggested, on the basis of artefactual evidence, that the area was operational between the 10th and 14th centuries AD (Buckley and Earl, 1990; McDonnell, 1993, 1994; Plate 8.1). The use of EDMA will therefore provide a definitive test to the efficacy of the technique in detecting signals associated with local mining and smelting activity. Crift Down may also have been a focus of activity during earlier periods (Gerry McDonnell, pers. comm.). The investigation therefore seeks palaeoenvironmental evidence for this hypothesis.

(iii) Results from the site will contribute to the sparse palaeoenvironmental database for the lowlands of south west England (Caseldine, 1983), and provide detailed information about the nature and scale of activity of the local populations during the Medieval period.

8.1 Site location and morphology

Crift Down is a spur of the St. Austell granite which forms a ridge running north west from the
Plate 8.1  The Crift Down area (view east).
The ridge forms part of the prehistoric trans-Cornwall communication route known
as the Saint’s Way. The archaeological excavation of the Medieval tinworking
remains is marked with an arrow.

Plate 8.2  The Crift Down sampling site (view north-west).
Figure 8.1 Location of Crift Down sampling site
town of Lanlivery. Helman Tor, a Neolithic walled settlement (Mercer, 1986) is found at the northern end of the ridge. The 'Saint’s Way', an important prehistoric trans-Cornwall communication and trade route runs southwards along the crest of the ridge towards Lostwithiel and the Fowey Estuary (Buckley and Earl, 1990; McDonnell, 1994).

The site investigated lies at an altitude of 144m OD. It is a soligenous valley mire bounded to the north and west by higher ground (Fig. 8.1; Plate 8.1). The present day vegetation is characterised by pasture grasses with *Crataegus monogyna* and *Corylus avellana* dominating the hedgerows, with a small patch of woodland immediately to the west (Plate 8.2). The site has been extensively drained for pasture since 1986, with the implementation of a land drain and associated sub-surface arterial pipes. A peat depth survey conducted revealed organic deposits to exist across the whole area, with a maximum depth of 1.80m (Burton, 1995). Two springs are located in the field, one close to the sampling site, the other to the south in the middle of the field. The position of these springs has maintained a high water table and is important in the accumulation of organic sediments in this location. The deepest sediments were encountered at the northern edge of the field, which was also the area least disturbed by drainage operations. The results seek to extend work carried out earlier (Burton, 1995; Burton and Charman, in press.) in a nearby location, with fine resolution pollen analysis and geochemical techniques used to fully establish the nature and scale of anthropogenic activity in this area of Cornwall.

### 8.2 Sampling regime

Samples were collected from the deepest point of the field (Fig. 8.1) using a standard Russian auger. Two samples were taken for radiocarbon dating. Each monolith was described in the field using Troels-Smith (1955) classification and subsequently re-examined in the laboratory to confirm initial identifications (Fig. 8.2). A total of 43 samples were prepared for EDMA, pollen, Total Organic Carbon (TOC), and ash content. Samples were taken at 5cm intervals, with fine resolution sampling of 2cm used between 55 and 70cm, and again between 100 and 110cm based primarily upon significant features in both the pollen and geochemical records.

### 8.3 Radiocarbon dating

Two samples were submitted to Beta Analytic for AMS radiocarbon dating. The samples were taken from levels in the core where cereal pollen increased (70 and 105cm) since this was assumed to be
related to definite human activity in the local area. The results of the dating procedures are given below in Table 8.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (cm)</th>
<th>Lab-code</th>
<th>$^{14}$C age</th>
<th>Calibrated age (BP)</th>
<th>Calendar age (ref AD 1950)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD70</td>
<td>70-71</td>
<td>Beta-098989</td>
<td>1030±50</td>
<td>1055-790</td>
<td>AD 895-1160</td>
</tr>
<tr>
<td>CD105</td>
<td>105-106</td>
<td>Beta-098990</td>
<td>2080±50</td>
<td>2145-1895</td>
<td>195 BC- AD55</td>
</tr>
</tbody>
</table>

Table 8.1 Radiocarbon dating results from Crift Down

Calculation of sediment accumulation rates is possible between the two dated levels, and gives a mean rate of 0.032 cm yr$^{-1}$. Assuming the top of the profile which includes 15 cm of sediment not investigated is modern, the accumulation rate for the upper 70 cm is 0.076 cm yr$^{-1}$. Assuming this rate is correct, the uppermost sample investigated in this study (15 cm) represents a date of ca. AD 1750. Extrapolation of dates for the sediment below 105 cm (195 BC-AD 55) is problematic, especially considering the possible truncation experienced at ca. 150 cm. The basal sediments could therefore date from the mid to late Mesolithic period on the basis of the palynological evidence (lacking significant quantities of Alnus pollen). This suggestion will be considered in more detail in the subsequent sections.

8.4 Palaeoenvironmental reconstruction of the Crift Down sediment

Discussion will be made initially of the stratigraphy of the sediment followed by the geochemical and pollen results. Multi-variate techniques were used, the results from which are presented at the beginning of the relevant sections.

8.4.1 Stratigraphical description

The basal unit is composed largely of a dark humified organic sediment in which fine rootlet material and some larger wood macrofossils were present, particularly evident at a depth of 160 cm (Fig. 8.2). The wood appeared to be that of Salix, but confirmation using reference material was not attempted. A sharp transition between the basal unit and the one lying immediately above suggests a possible depositional hiatus at 150 cm. The overlying unit is composed of black, very well humified organic material, again with fine root fragments visible, but with a complete absence of larger macrofossil elements. The sediment between 72 and 126 cm is again a well humified organic material, slightly
Well humified light brown organic material with modern root penetration evident. Abundant siliceous particles visible, with occasional clasts up to 5mm in diameter.

Light brown humified organic matter. Very fine rootlets. Lack of mineral material.

Light brown/orange unit dominated by well preserved moss macrofossils.

Dark brown humified sediment with infrequent identifiable macrofossil components. Fine plant fragments with sand/silt particles visible.

Light brown humified organic matter. Very fine roodets. Lack of mineral material.

Well humified dark brown organic material with frequent mineral particles evident.

Black humified organic material with no visible macrofossil remains.

Dark humified unit with fine root fragments and some larger wood macrofossil components (+).

Figure 8.2  Stratigraphy of the Crift Down sediment
lighter in colour than that of preceding levels. The most significant feature of this material is the increased frequency of mineral particles, with a layer of sand at 114cm. The next stratigraphic unit displays abundant mineral matter, and consists of dark brown humified sediment with infrequent macrofossil components of *Sphagnum* and monocotyledonous fragments. The unit between 42 and 50cm appears quite different from units further down the profile. It is a light brown/orange colour with well preserved *Sphagnum* macrofossils. A similar unit is encountered at a depth of 32-42cm, but is composed of more humified material with abundant fine rootlets. The uppermost unit is composed of a well humified light brown organic material, which displays evidence for modern root penetration, and abundant mineral particles (up to 5mm in diameter). It was not possible to sample the top 15cm due to the friable nature of the sediment and the increased evidence for disturbance in the upper sedimentary horizons.

8.4.2 **EDMA investigation of the Crift Down sediment**

The EDMA results are presented as element profiles (Fig. 8.3a,b) divided into five distinct chemizones, which are summarised in Table 8.2. Initial indications suggest the profiles for a number of elements to be of limited use, since they display inter-correlated profiles, as seen for a number of other sites so far investigated. It seems that the close similarity between the profiles of Pb and Mn confirm this to be a distinct possibility. Further discussion will be made of this later in this chapter and in Chapter 9.

8.4.3 **Multi-variate analysis of the Crift Down EDMA data**

DCA of the geochemical data produced two plots (Figs. 8.4 and 8.5). It seems that axis one of Fig. 8.4 indicates the mineral/organic matter continuum, with Si and %ash located on the extreme left and the elements associated with organic sedimentation on the right (TOC, S and here Ca). Axis two seems to represent an acidity gradient with those elements collectively indicative of high base conditions present on the bottom (Na, Mg, K and Fe) with the more acidic elements present towards the top of the plot. It is significant to note, however, the position of Sn. This element does not show an association with any other group, including the other heavy metals, indicating possibly a more useful geochemical signal for this element from this particular sedimentary environment.

The sample plot (Fig. 8.5) produced five groups, the first of which (group one) includes the basal samples between 150 and 168cm, although the designation of this group in its own right is
EDMA results from Crift Down sediment
<table>
<thead>
<tr>
<th>Chemizone</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDGa</td>
<td>168-147.5</td>
<td>A number of elements display dynamic equilibrium with a declining trend: Si, Fe and K. S and P display profile peaks in this zone. The trace elements, Sn, As with Mg display static equilibrium conditions. Dynamic metastable equilibrium conditions with a threshold at 150cm mark the boundary between CDGa/b; this is particularly illustrated by changes for S, P, Si, Mn, Ca, K and TOC. The ash content of the sediment in CDGa is relatively constant at ca. 40%.</td>
</tr>
<tr>
<td>CDGb</td>
<td>147.5-122.5</td>
<td>K, Pb and Si display increased amounts with respect to the preceding zone. P, Fe and Na seem to take longer to recover, increasing gradually to the upper boundary level. Sn, As and Mg are present in negligible quantities. S, Ca, K and TOC demonstrate declining dynamic equilibrium conditions, the former two elements decline to low amounts for the rest of the profile by the CDGa/b boundary. The zone displays high and increasing ash values.</td>
</tr>
<tr>
<td>CDGc</td>
<td>122.5-72.5</td>
<td>Ca and S decline to low amounts, similarly K and Al fall through the zone. Fe remains stable in this zone. Mn and Pb display a change in equilibrium level at 110cm. Si and P generally increase through the zone, although the latter element decreases from 4 to 2% between 70 and 90cm. As and Sn display low stable conditions. A number of elements fluctuate in this zone e.g. Cu, Na, Mg and ash values. Na displays a declining trend through the zone.</td>
</tr>
<tr>
<td>CDGd</td>
<td>72.5-56</td>
<td>Stability is indicated by the majority of elements here: Ca, Mg, Pb, Si, S and As. K increases to a peak in the upper samples of the zone. Al displays a declining profile, with Fe gradually increasing to ca. 6% at 56cm. The key feature of the zone is the fluctuations exhibited for Sn, with a number of peaks identified at 61, 65 and 69cm. The ash content of the sediment falls between ca. 60 and 70cm and remains stable at 50% for the rest of the zone.</td>
</tr>
<tr>
<td>CDGe</td>
<td>56-15</td>
<td>Fe and K increase to profile peaks in the upper sample of this zone. A number of elements display stable equilibrium conditions: Mn, Pb, Si, S, Sn, Cu. Peaks for As are noted at 30 and 42cm. TOC fluctuates through the zone, but recovers marginally in the upper sample. Al increases to a zone peak of ca. 17% at 42cm, then falls steadily in the remaining samples.</td>
</tr>
</tbody>
</table>

Table 8.2 Description of the chemizones from EDMA of the Crift Down sediment
Cumulative percentage variance explained by two axes = 85.6%

Figure 8.4  DCA element plot of EDMA data from analysis of Crieff Down
Cumulative percentage variance explained by two axes = 85.6%

Figure 8.5  DCA sample plot of EDMA data from analysis of Crift Down sediment
questionable since it clearly displays much internal heterogeneity. These samples are however sufficiently different from the others to place them on the far right of the DCA plot. The next four groups are all closely positioned on the plot, but clear and tight clustering of sample depths make it possible to differentiate a number of assemblages. Group two includes samples between 125 and 145 cm. The next group (three) includes a number of samples which range in depth from 70 to 115 cm. This group is closely related to a tightly clustered assemblage (group four). The final group (five) includes the uppermost samples and indicates the most recent activity in the area.

8.4.4 Interpretation of the geochemical signals from Crift Down

Analysis of the sediment from Crift has made it possible to interpret the signals in terms of a number of specific processes and environments, these will be discussed in chronological order below.

Fen conditions in the basal sediment

The basal zone from Crift Down is dominated by peaks for S, P, Ca and high levels of TOC. Elevated levels of S indicate the production of sulphides in the anaerobic zone (Rudd et al., 1986). Declining amounts of Fe confirm the presence of base rich groundwater, but suggests the developing anoxic status of the sedimentary system since this element is commonly mobilised under acidic, anaerobic conditions (Goldschmidt, 1954; Mackereth, 1966; Engstrom and Wright, 1984; Naucke et al., 1993).

Decreases noted for Si and K through zone CDGa suggest the reducing input of material from external sources, confirmed by the generally low levels of ashed material in these levels. There is no relationship between the indicators of physical erosion, Na, K, Ca and Mg, and it is therefore likely that autogenic processes account largely for their geochemistry here. High levels of Ca seem to corroborate the importance of autogenic processes in this zone, and it therefore seems possible that the greatest proportion of Ca is complexed with organic ligands (Goldschmidt, 1954; Engstrom and Wright, 1984). This suite of elements provide further confirmation for the presence, but declining importance, of base rich groundwater circulation. The conditions experienced in the basal 20 cms seem indicative of a fen environment, in which sulphides form in the permanently saturated anoxic sediment as the sedimentary environment becomes progressively acidic to CDGb.
A possible depositional hiatus

The boundary separating CDGa and CDGb is sharp and either indicates a hiatus or a rapidly changing environment. The potential hiatus is illustrated by a number of elements, and is shown as a threshold separating dynamic metastable equilibrium state for a number of elements (Butzer, 1982). Those elements particularly effected are S, P, Ca, K and Si. Clearly, the geochemical situation indicated by CDGb is different from the environment illustrated by the signals of the preceding zone. It seems the system becomes progressively oxidised, with a low, declining trend for S, indicating the cessation of sulphide formation in a progressively aerobic sedimentary environment.

The indicators of physical erosion seem more abundant in this zone with high levels of K, Na and Al, all of which may be considered indicators of the introduction of clastic material to the sedimentary system (Engstrom and Wright, 1984). The notion of increasing mineral matter in this zone is again corroborated by the increased levels of ash. Increasing Si may indicate a number of different environmental processes such as erosion of exposed soils, inclusion of wind-blown dust (Cowgill and Hutchinson, 1970), and/or associations with alumino-silicate minerals. However, the lack of correspondence between Al and Si questions the last suggestion. The elevated levels of Si in conjunction with increasing Fe may relate to the influence of groundwater circulation, and would similarly explain the higher level of K in CDGb, the possible increase in pH and diminished production of sulphides.

Geochemical stability

The next zone (CDGc) indicates stability for a number of elements suggesting a relatively stable environment, with no major disturbance episodes. Low levels of S suggest the continued aerobic status of the sedimentary system, with only minimal production of sulphides, possibly in very locally anaerobic situations around root nodules where microbial mineralisation is active. However, the declining profile for TOC suggests gradually increasing catchment disturbance, with increases for ash noted. Decreasing K, Na and Al most likely suggest the diminished influence of groundwater circulation, with the effect of lower pH levels due to the increased effect of organic acids which are no longer leached through the system. The presence of P possibly indicates the continued oxidised status of the sedimentary system, since this element is noted as having a very low solubility under such conditions. Shotyk (1988) comments that the capacity of peat to uptake P is essentially a function of the mineral content of the organic material.
High levels of Si can relate to a number of different processes, but increases in the upper samples of CDGe may be associated with the presence of diatoms at 60cm or the inclusion of locally derived mineral matter. The return to groundwater circulation is indicated by the elevated levels for Fe above 60cm and indicates the vertical limit of the modern surficial oxygenated environment. The low, stable profile for S indicates the higher base status of the system at this time; the increasing levels of Ca and K further confirm this suggestion.

Evidence for Medieval industrial activity

The most significant feature of this zone (CDGd) is the elevated levels for Sn identified at 61, 65 and 69cm. Since there is no significant indication of increased physical erosion in this zone (relatively stable ash and clastic elemental profiles), and the element does not exhibit any clear associations with other elements, it is possible to suggest that the Sn is not a direct component of local detrital mineral material. It is likely that the element was derived largely from the operations of the processing plant ca. 200m to the north-east (McDonnell, 1993). The occurrence of Sn in peat systems will result primarily from exploitation of the metal (Goldschmidt, 1954). Although little information on the geochemistry of Sn is available, it seems likely that the metal may have been chelated as an organo-metallic complex (Beeson et al., 1977; Edwards et al., 1995). High amounts of ash in this and preceding zones, ranging from 40 to 80% clearly exceed the technical definition of 'peat' which contains no more than 25% by weight mineral matter (Andrejko et al., 1983). The ash content in all zones above 150cm exceed the values for fen peats reported by Naucke (1980), suggesting that much of the mineral matter was deposited as suspended material carried by locally flowing streams and/or from the near-by spring. The Sn in these levels is therefore likely to have been carried in water either discharged directly from the tin processing site, or from near-by alluvial workings, rather than from aerial smelting pollution.

Recent geochemical signals

CDGe indicates surficial enrichment for a number of elements. Potassium attains high levels in the zone which relates to the processes of bio-accumulation (Shotyk, 1988) since it is an important plant nutrient in peatland ecosystems (Naucke et al., 1993). Iron similarly exhibits elevated values in the upper portions of the profile, which most likely relate to the oxidised nature of the peatland system. This condition in the sedimentary environment explains the low presence of sulphide compounds in the upper zones. The heavy metals are all low and stable suggesting either low, but continued input,
or the presence of the elements close to the detection limits of the analytical technique. Tin is low and the signal possibly reflects background concentration as suggested above. This would suggest that either the tinworking activity was confined to the Medieval period only, between the 10-14th century AD (McDonnell, 1993), or subsequent activity was on a much smaller scale. The presence of two peaks of As in the upper zone pose several questions. Does the presence of the metal indicate the smelting of Sn as suggested by Harris (1992), and if so why was it not represented in the preceding zone? It may be that the As peaks do in fact relate to the smelting of tin, but that technological improvements had reduced the levels of Sn lost in the flue dust/soot or drainage waters, although this is open to much speculation.

8.4.5 Pollen analysis of the Crift Down sediment

The palynological investigation of sediment from Crift has great potential to reveal much information about the activities of the population at a lower altitude site than was possible from the previous Dartmoor sites. Specific activity relating to tin extraction and processing operations may be detectable including deforestation, and the production of arable crops. The results are presented as a pollen diagram (Fig. 8.6) and summarised in Table 8.3. The data are shown as percentages of Total Land Pollen (TLP).

8.4.6 Multi-variate analysis of the Crift Down pollen data

DCA plots from this analysis of the data are presented as a species plot (Fig. 8.7) and a sample plot (Fig. 8.8). Analysis of the species data (Fig. 8.7) reveal three groups: α, β and χ. The first indicates woodland conditions with the majority of arboreal species represented, including Quercus, Pinus, Betula, Ulmus, Salix and scrub components, Corylus avellana and Hedera helix. A large group (β) relates to the extensive and well represented herbaceous flora of the area which expands significantly through the pollen profile. Species present are representative of disturbed habitats, including indications of arable cultivation. The last group (χ) includes a small number of species particularly associated with damp conditions.

The sample plot (Fig. 8.8) includes three assemblage groups. The first (I) include those species between 150 and 168cm, which strengthens the proposition made earlier for a depositional hiatus at 150cm since these samples are sufficiently different to isolate them from those remaining on the DCA plot. The second group (II) indicates the transitional environment in which arboreal pollen
Figure 8.6  Crift Down percentage pollen diagram
Exaggeration factor x10, + indicates a trace occurrence (<1% TLP)
<table>
<thead>
<tr>
<th>LPAZ</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
</table>
| CD1  | 168-147    | *Salix, Corylus avellana*-type, Pteropsida, Cyperaceae  
*Salix* dominates AP (>30% TLP), smaller amounts of other arboreal species are detected. *Corylus* is abundant. The herbs are composed almost exclusively of members of the Cyperaceae family. Varying fern species are present including *Osmunda regalis*, *Polypodium* and *Pteridium aquilinum*. |
| CD2  | 147-117    | *Alnus, Corylus avellana*-type, Pteropsida, Cyperaceae  
*Alnus* dominates the spectra, appearing suddenly at 145cm, again suggesting a truncated profile. *Salix* correspondingly disappears. *Corylus* is still present, but not so abundant as in CD1. *Cyperaceae* dominates the NAP spectra, but more herbaceous species are present albeit in trace quantities. A peak in the number of Pteropsida spores encountered occurs at 125cm. A significant peak in charcoal fragments similarly occurs at this level. |
| CD3  | 117-67     | *Alnus, Corylus avellana*-type, Pteropsida, Poaceae  
*Alnus* once again dominates the arboreal pollen spectra, but Poaceae expands significantly. Members of the Cyperaceae family are present in relatively constant amounts (ca. 15% TLP). Herbaceous components expand significantly including *Plantago lanceolata*, *Potentilla*-type and members of the Lactuceae tribe of the Asteraceae family. Cereal pollen is first detected at 105cm. Sustained, high levels of charcoal are observed throughout this zone. |
| CD4  | 67-15      | *Alnus, Pteropsida, Poaceae, Cyperaceae, P. lanceolata*, Lactuceae  
*Alnus* still dominates AP, but in a reduced extent. The pollen spectra of this zone are dominated by Poaceae and Cyperaceae, with an increased presence of *P. lanceolata*. Arable weeds are present in the upper levels of the profile associated with the final peak of Cereal type pollen. *Pteridium aquilinum* dominates the spore count. An increased presence of Potamogetonaceae undiff. is noted in the upper 50cms of sediment. |

Table 8.3 Description of LPAZ from pollen analysis of Crift Down sediment
Figure 8.7 DCA species plot of pollen data from analysis of Crift Down sediment (Species shown all have occurrences >1% TLP in >5 samples)
Figure 8.8 DCA sample plot of pollen data from analysis of Crift Down sediment

Cumulative percentage variance explained by two axes = 50.3%
declines and is replaced by the herbaceous species of group \( \beta \). The final assemblage (group III) illustrates the conditions revealed by the uppermost samples, between 15 and 80cm. It seems likely that axis one on Fig. 8.8 indicates a continuum in which increasingly open local conditions are encountered as the samples progress towards the axis two.

### 8.4.7 Interpretation of the Crift Down pollen data

#### Basal fen conditions

The bottom levels of the profile indicate a *Salix* fen woodland community dominating the local environment. A range of herbaceous and pteridophyte taxa indicative fen communities are present including *Filipendula*, members of the Cyperaceae and Chenopodiaceae families, *Lysimachia vulgaris* and *Osmunda regalis*. Huntley and Birks (1983) note *O. regalis* to tolerate wet conditions, its favoured habitats including fen woodlands, fens and ditches. The surrounding environment is composed of large areas of relatively open land characterised by a *Corylus avellana* dominated flora with a significant pteridophyte component. A difficulty arises with the identification of *Corylus avellana* in such an environment. It is likely to include a component of *Myrica gale* since the pollen of the two species is inherently difficult to differentiate solely on the basis of morphological features of the grain (Godwin, 1975; Edwards, 1981). It is likely that both species would have been present in this sort of environment, perhaps with *C. avellana* restricted to the drier slopes above the 160m contour, while *M. gale* would have been present in the damper areas (Stace, 1991).

The low pollen values recorded for *Quercus* and *Betula* in the basal samples serve to indicate a number of possibilities: (i) either the dense fen woodland imposes a strong pollen filtering effect which limits the amount of pollen falling onto the surface of the mire; (ii) the low concentration of pollen for these species reflects the low presence of the two species in the local environment; or (iii) the low pollen concentration indicates the presence of an area of undetermined woodland size composed primarily of these two species but at some distance from the developing mire (Tinsley and Smith, 1974; Jacobson and Bradshaw, 1981).

#### Increasing anthropogenic activity

The boundary between *CD*1/2 is marked by a very sharp change in a range of different pollen types and as such is interpreted as a depositional hiatus. However, *CD*2 indicates an environment representative of the natural seral succession from *CD*1 (cf. Walker, 1970). The environment seems
to have succeeded the *Salix* fen of the preceding zone and now indicates an *Alnus* dominated woodland with minor components of *Frangula alnus* and *Betula*, although the latter may also be an element of the open *Quercus* woodlands. *Salix* is still present, but the dominance of *Alnus* may be due to the difference in reproductive strategies between the genera and possibly a greater pollen production capacity. *Alnus* favours water-borne seed dispersal strategies, with the capacity for seeds to survive long periods of waterlogging (McVean, 1956), which would be a distinct advantage in such an environment. A range of herbaceous taxa support the continued presence of a fen woodland community, including *Filipendula*, and members of the Cyperaceae, Chenopodiaceae and Caryophyllaceae families.

*CD2* includes the first evidence for disturbed conditions, suggesting either disturbance of the fen woodland itself, or clearance of the woodland communities adjacent to the mire. Tentative evidence exists to support both of these hypotheses. Declining *Quercus, Betula* and the disappearance of *Ulmus* with increasing amounts of fern spores indicate the presence of a more open environment, although the high levels of *Alnus* pollen will greatly affect the spectra of the less abundant species. However, high amounts of charcoal in *CD2*, in particular the peak at 135cm (4.8x10^6 fragments ≤180mm cm^-3), seems to corroborate the presence of fire activity in the locality.

The higher area surrounding the site displays evidence for a sparse cover of *Corylus avellana*, but includes increasing heathland components. This suggests the increasing acidity of local catchment soils, possibly due to processes such as increased clearance activity (Hatton, 1991).

The next zone (*CD3*) indicates a complex mosaic of plant community types in the local environment and more regionally. The continued, but diminishing, presence of *Alnus* confirms an area of fen type habitats. Again, this is associated with smaller components of *Salix* and possibly *Betula*, and herbaceous species indicative of damp fen communities such as *Filipendula*, members of the Chenopodiaceae, Cyperaceae and Caryophyllaceae families and *Chrysosplenium*. The last species is generally suggestive of damp, shaded conditions (Godwin, 1975), and is a low pollen producing, entomophilious herb. Its representation in the spectra of *CD3* illustrates the more open nature of the fen woodland at this time. The falling values for *Alnus*, and declines for the fern species suggest they may have formed components of the same community. Evidence exists for the presence of wetter conditions around 80cm with increases in *Chrysosplenium* and *Hydrocotyle vulgaris*. 247
The Medieval landscape of Crift Down

Evidence exists for the presence of small relatively open areas of deciduous woodland composed primarily of *Quercus* and *Betula*, with smaller elements of *Ulmus*, *Fagus sylvatica*, *Carpinus betulus* and *Tilia cordata*. Low levels of *Corylus* (<15% TLP) may either relate to these woodland patches, since it is frequently encountered as an understorey shrub, or as a component of the higher slopes along the Saint's Way and on the southern flanks of Helman Tor (Fig. 8.1). The species would have formed a local component of the rapidly expanding grassy heathland communities likely to have existed in this area.

While Poaceae dominates the pollen spectra of CD3, there appears to be two distinct grassland communities indicated. Firstly, a pasture-type flora including members of the Fabaceae family (possibly *Trifolium* and *Lathyrus* species), with *Lotus* spp., *Plantago lanceolata*, *Ranunculus* acris-type, and components of the Lactuceae tribe and Apiaceae family. These species commonly form components of meadows and pastures, and are highly resistant to grazing (Godwin, 1975; Behre, 1981). Similarities exist between this flora and the range of taxa present in damp and dry meadow communities: class Molinio-Arrhenatheretea (Rieley and Page, 1990). Although it is difficult to be precise with respect to the presence/absence of a specific species in a community using palynological techniques alone, the presence of the above species in CD3 suggest the local presence of meadow communities.

Secondly there is evidence for arable activity, with such species as *Centaurea nigra*, which is often associated with prehistoric clearance activity and agriculture (Godwin, 1975), and is most frequently recorded in ungrazed neutral grasslands that are maintained by agricultural practices (Grime et al., 1988; Rieley and Page, 1990). Species including *Urtica dioica*, *Achillea*-type and members of the Lactuceae tribe may be present as arable weeds, along with some members of the Fabaceae family. However, the most significant evidence for arable cultivation is the presence of Cereal type pollen grains at 70, 85 and 100cm with extrapolated dates of ca. AD 1030, 600 and 90 respectively. This confirms the general continuity of human activity in the vicinity for around 1000 years before the Medieval archaeological evidence associated with tinworking at Crift. Over this period of time the environment has become progressively more open with a significant expansion in the floristic diversity of the herbaceous species represented, and increased evidence for the use of fire as a tool (Fig. 8.6).
Continued Medieval activity: a mosaic of habitat types

The final zone of the Crift Down profile (CD4) suggests a predominantly open grassland dominated environment. The *Alnus* fen woodland is shown to diminish in extent, indicating the more open nature of the area. The lower levels of *Alnus* in the zone may relate to use of this tree for charcoal production (Chambers and Price, 1985) for the smelting of tin at the nearby industrial complex located ca. 200m north east of the sampling site (McDonnell, 1993, 1994). Small areas of woodland may exist, composed of *Quercus* and *Betula*. Further clearance of *Corylus avellana* on the higher, drier areas is noted, accompanied by an expansion of heathland areas and the arrival of *Ulex* species. This is a major component of the modern day flora around the lower slopes of Helman Tor. However, it is difficult to suggest the abundance of this entomophilous shrub on the presence of pollen data since little work has been conducted on its flowering and dispersal capabilities (Anderson, 1967, 1974). It is also possible that *Ilex* may have formed a component of this scrub environment, but it may also have formed an element of the increasingly open fen woodland communities.

The continued presence of grassland dominated areas including both the pasture and arable elements of CD3 are noted. However, the increased presence of cereal pollen grains is significant since these grains are generally under-represented in records derived from peatland areas (Behre, 1981). Indeed clumps of this pollen type were encountered at 65cm suggesting the very local presence (Moore et al., 1991) of cereal cultivation and/or processing operations (Hall, 1988). The arable weed flora becomes more developed than that represented previously in CD3, including such species as *Fallopia* (most likely *F. convolvulus* - see Bennett et al., 1994), which is a reliable indicator of arable activity (Behre, 1981), and *Polygonum* (*P. aviculare*) common in similar habitats (Godwin, 1975). *Artemisia*-type includes a few species (e.g. *A. vulgaris, A. campestris*) associated with anthropogenic disturbance, in particular arable cultivation (Huntley and Birks, 1983). Behre (1981) suggests *Rumex acetosella* is more a component of arable fields than simply a result of clearance activity. This is significant since the species first becomes evident in the pollen spectra of CD4. Similarly *Jasione montana*-type frequently appears with weeds typical of arable cultivation (Godwin, 1975), and associated fallow periods (Behre, 1981).

It seems likely therefore that by CD4 the area around Crift Down was virtually open except for small pockets of deciduous woodland, possibly at some distance, with a diminishing *Alnus* fen woodland, and a small localised scrub component on the higher areas. The expansion of arable cultivation is
illustrated by the increased presence of cereal pollen grains, and a more diverse arable weed flora.

The uppermost sample has an extrapolated radiocarbon age of ca. AD 1750. This date suggests the continuity of arable activity and indeed the presence of human populations in the area from pre-Medieval times. The increased evidence for a more developed arable flora serves to indicate the possible use of the sampling site for crop production.

8.5 Discussion of the palaeoenvironmental development of the Crift Down area (Table 8.4)

The basal levels of the profile indicate a high nutrient status closed canopy willow fen environment. Geochemical data suggest the sedimentary system was oxidised but was becoming progressively anoxic, allowing the formation of sulphides. The initially high nutrient status of the system is indicated both by the components of the flora (e.g. *Osmunda regalis*), and the geochemistry of the sediments, with high levels of Fe and base elements suggesting the circulation of base rich groundwater. However, the reduction of Fe towards CDGb serves to reinforce the increasingly anaerobic status of the system and the lowering pH. The low levels of charcoal in this zone illustrate the general absence of anthropogenic disturbance in the area at this time. It seems likely that these sediments date from the late Mesolithic period due to the general absence of *Alnus*, a species usually present in lowland sites by 5000 BC. A depositional hiatus was identified both stratigraphically, and using pollen and geochemical analysis. Changes in a number of taxa, particularly *Alnus* and *Salix*, and elements, namely S, P, Ca, K, Si and TOC, were instructive in confirming the presence of a truncation at 150cm.

The duration of this hiatus is extremely difficult to establish without further radiocarbon evidence. However, the pollen data indicate the continued presence of fen communities at the site but a change in the dominant species from *Salix* to *Alnus*. This change is characteristic of the natural sequence of seral succession in this type of wetland environment (Walker, 1970). Clearly the geochemical conditions associated with this phase of fen woodland are quite different from that of the preceding zone. The system seems to become progressively oxidised with increasing amounts of Fe, an element ubiquitous in oxygenated environments, and lower levels of S. The indicators of physical erosion are better represented in this zone, which agrees with the results of the pollen analysis indicating increased disturbance of both the fen woodland and the surrounding tree cover. The nature of the clearance is difficult to ascertain from the available evidence, but increased concentrations of
<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Date</th>
<th>Geochemistry</th>
<th>Vegetation</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>ca. AD 1250</td>
<td>Aerobic sedimentary environment (Fe), increased base status (K, Ca).</td>
<td>Sparse woodland, developed arable flora.</td>
<td>Open grassland dominated environment.</td>
</tr>
<tr>
<td>70</td>
<td>Medieval AD 895-1165</td>
<td>Increased levels of Sn detected.</td>
<td>Low AP, high charcoal values.</td>
<td>Industrial activity. Active deforestation of local woodland resources. Opening environmental conditions. Increased evidence for arable cultivation and pastoral activities.</td>
</tr>
<tr>
<td>85</td>
<td>AD 600</td>
<td>Stable profiles for a number of elements: K, Na and Al.</td>
<td>Lower levels of AP, spectra dominated by Poaceae.</td>
<td>Declining local woodland, increasing evidence of arable activities.</td>
</tr>
<tr>
<td>100</td>
<td>Romano-British AD 90</td>
<td>Aerobic sedimentary environment.</td>
<td>High levels of <em>Alnus</em> and fen species.</td>
<td>Arable activity, Increasing charcoal concentration, declining arboreal pollen suggest disturbance to the local woods.</td>
</tr>
<tr>
<td>150</td>
<td>Late Mesolithic (post 5000 BC)</td>
<td>Aerobic sedimentary environment.</td>
<td><em>Alnus</em> dominated local fen woodland, increasing Poaceae.</td>
<td>Opening environment, expanding grassland areas.</td>
</tr>
</tbody>
</table>

Table 8.4 Summary of the palaeoenvironmental conditions of Crift Down

251
 charcoal suggest the active use of fire. The increased base status of the system at this time is indicated, and possibly relates to increased circulation of groundwater, or increased levels of runoff from the local slopes. Clearance activity is generally associated with increased throughfall, itself contributing to a greater overland flow component and thus an enhanced catchment erosion yield, and increased leaching of solutes from the surrounding slopes. The eroded material would have been transported downslope and a proportion of it may have been deposited onto the mire surface causing a temporary amelioration in base status. Continued clearance is postulated, since arboreal pollen is shown to fall progressively, with an associated increase for grassland communities. However, lower levels of detrital clastic material are indicated by the reduced levels of K and Al. Continued oxidation is illustrated by the sediments of CDGc, with a lower pH which may relate to the increased presence of heathland species on the slopes around the mire.

The key feature of the geochemical profile from Crift Down is the Sn peaks between 56 and 72cm. Although the geochemistry of the element in peatland systems is little known, it seems fair to suggest that the activity is linked with the processing of tin at the site upslope. Archaeological excavation has suggested a Medieval date for the activity, probably between the 10th and the 14th centuries AD (Buckley and Earl, 1990; McDonnell, 1994). This date fits well with the arable activity indicated by the pollen data, itself most likely attributable to the strip field system of the later Medieval period (Preston-Jones and Rose, 1986).

The sedimentary system at this time seems to be experiencing a higher base status, possibly relating to an increasing component of eutrophic water from the nearby spring. Increases for Fe may be considered indicative of increased groundwater influence (Chapman, 1964; Green and Pearson, 1977; Mannion, 1979). The presence of Hydrocotyle vulgaris similarly indicates the proximity of eutrophic water (Godwin, 1975; Stace, 1991). The upper zones of the profile indicate expansion of grassland communities, with a developing arable and pastoral component. The presence of scrub and heathland is confirmed on the upper slopes. The geochemical signals are dominated by the complex physical, biological and chemical processes operational in the acrotelm of the system, but do however seem to indicate oxidised conditions.

The next chapter will discuss the general applicability and reliability of EDMA in palaeoenvironmental studies with reference to the results so far presented. Critical analysis of the
information obtained from EDMA for the heavy metal elements will be made with reference to the investigation of selected sediments from Tor Royal and Crift Down using a complementary geochemical technique.
9.0 Introduction

This research sought to examine the usefulness of EDMA in the analysis and interpretation of palaeoenvironmental change in south west England. The technique was initially considered attractive for this type of study due to the speed and non-destructive nature of the analysis, and the use of only small amounts of sediment. The project thus aimed to evaluate the efficacy and accuracy of the technique to provide interpretable data from a number of different sediment types, each with material derived from a variety of sources, and reflecting processes operational at a range of spatial and temporal scales.

The main thrust of the research was therefore to examine the potential utility of EDMA as a standard palaeoenvironmental research tool by applying the technique to a range of 'real' palaeoenvironmental situations. This required the comparison of results obtained from EDMA to those gained from standard geochemical methods to establish the reliability of the method, as described in Chapter 3, and the application of EDMA at a number of different sites in south west England (Chapters 4, 5, 6, 7 and 8).

Results from this research provide a unique opportunity to investigate palaeoenvironmental conditions of the peninsula using a more holistic approach based mainly upon geochemical and palynological data. The pollen evidence is an extremely valuable source of data providing information on the impacts occurring and the timing of various events. Geochemical data reveals information relating to the different accumulation phases of the peatland systems and the associated autogenic signals, but has the greatest potential in palaeoenvironmental studies to provide information relating to processes external to the peatland such as disturbance created by deforestation episodes and mineral processing activities.

9.1 EDMA in practice

The results from North Sands (Chapter 4), provided an insight to the processes of sea-level change in the Kingsbridge Estuary. The basal sediments are characterised by terrestrial *Typha* swamp conditions, there is then increasing evidence for marine conditions between 9 and 11m associated
with the deposition of significant amounts of mineral material. Increasing signals for autogenic activity (S, TOC) are present above 9m. In the upper portions of the profile Si and Al are predominantly linked to alumino-silicate material from erosion of the local catchment materials.

Results from sites on Dartmoor reveal much information relating to palaeoenvironmental conditions operational at different temporal and spatial scales on this upland area. Analysis of the material from Tor Royal (Chapter 5) suggest the basal sediments accumulated around 5500 BC in an environment characterised by relatively intensive landscape disturbance, illustrated by the concentration of alumino-silicate mineral matter below 550cm. EDMA results suggest the system to have been acidified from the mid-Holocene onwards with the geochemistry of the upper levels dominated by processes operational within the sediment body itself. The uppermost levels display indications of acrotelm activity with bio-accumulation and precipitation of a number of elements, in addition to increased levels of presumably wind-blown mineral material. Analysis of the other Dartmoor sites provides information of a much more local nature, due mainly to the topography of the surrounding catchment areas. Merrivale (Chapter 6) has basal sediments characterised by increasing catchment disturbance, culminating in a significant episode at the Iron Age/Romano-British transition which seems linked to local deforestation activity. The results from a multiple core study of the area around Piles Copse (Chapter 7) suggest that correlation between geochemical signals from different sedimentary systems is problematic since autogenic processes seem far more important in controlling and explaining the majority of elements investigated. The Dartmoor sediments do not reliably present the signals linked with mineral extraction and processing activities, for which much archaeological evidence exists throughout the upland area. Discussion of this problem will be made in section 9.2 below. Clearly, the utility of EDMA for analysis of heavy metals from peatland sediments must be questioned.

The results from Crift Down (Chapter 8) provide a valuable insight into the development of this area. Archaeological evidence in the vicinity suggests the site to have been an important tinworking centre during the Medieval and possibly earlier periods. Geochemical analysis identified the levels to which this activity relates and these were confirmed by AMS radiocarbon dating. Increases for Sn in these levels suggest EDMA is possibly capable of detecting higher levels of heavy metal pollution in certain situations.
EDMA has allowed investigation of general episodes of environmental change. The most significant information is obtained when the assemblage of elements detected is considered, with the interpretation of individual elements generally of limited utility. With this in mind the following discussion summarises the results from the geochemical analysis of the sites with respect to a number of different environmental processes, operating at different scales (allogenic, autogenic and post-depositional), although it must be stated that the processes may not always have been mutually exclusive. Table 9.1 introduces the interpretation possibilities based upon the experience of analysis of the sites from south west England. It must be noted that individual elements may be interpreted differently depending on their trends, abundance and the other elements with which they occur.

A potential problem inherent to EDMA and the way in which it produces data occurs when an element is in low concentration in the sediment, typically the base and heavy metal elements, particularly when more abundant elements dominate the samples (often Si, Al, Fe and S). The representation of elemental data as percentages (of the total values for all elements chosen) can create problems since the more abundant elements may effectively reduce the values for less abundant components, the apparent fluxes of these minor elements simply relating to changes in the more abundant elements. This is one of the possible explanations for the unreliable data obtained for the heavy metal elements in this study and will be discussed more fully below.

**Allogenic group**

This group of elements are the most significant in palaeoenvironmental research since it is usually changes external to the sedimentary system that are of most interest. These elements are linked to processes operating at a range of different spatial scales, but are always associated with the introduction of material to the system from an external source. EDMA results indicated that elevated levels of Si and Al when associated with %ash relate usually to the introduction of alumino-silicate materials to the sedimentary system. However, in certain situations Al seems to have been linked to humic/fulvic materials (e.g. Merrivale and possibly Piles Copse and Crift Down) which may be connected to the levels of DOC (Muscutt et al., 1993). However, an assemblage including Si, Al, Ca, K, Na and Mg is similarly linked to an erosion episode in which material is transported to the sedimentary system, as was seen in the basal samples from Tor Royal and in the upper chemizone, TRGf, and from the sediments at North Sands (NSGb and NSGf), but may indicate the erosion of soil material as opposed to granitic basement fragments.
<table>
<thead>
<tr>
<th>Element</th>
<th>Interpretation based on EDMA data</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Allogenic</strong></td>
<td><strong>Autogenic</strong></td>
</tr>
<tr>
<td>Si</td>
<td>When associated with Al and %ash = mineral material</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>When associated with Si and %ash = mineral material</td>
<td>When associated with S and TOC = humic/fulvic material</td>
</tr>
<tr>
<td>Na</td>
<td>When associated with %ash = mineral matter</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>When a relationship exists between Na, K, Mg, Ca, Si and Al this elemental assemblage suggests the presence of soil material</td>
<td>Possibly linked to the circulation of groundwater, particularly when linked to Fe</td>
</tr>
<tr>
<td>Mg</td>
<td>Climate change if related to Na and evidence for increased accumulation of sediment. Marine influence</td>
<td>Humic/fulvic material</td>
</tr>
<tr>
<td>Ca</td>
<td>Erosion: transportation as oxides/oxide coatings on mineral material; soil material</td>
<td>Redox status of sedimentary system: aerobic</td>
</tr>
<tr>
<td>Fe</td>
<td>Erosion: transportation as oxides/oxide coatings on mineral material; soil material</td>
<td>Redox status of sedimentary system: aerobic</td>
</tr>
<tr>
<td><strong>Heavy metals</strong></td>
<td>Formed of sulphides under anaerobic conditions</td>
<td></td>
</tr>
<tr>
<td>(Sn)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cu)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Redox status of sedimentary system: anaerobic, especially when associated with TOC</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.1 Summary of the interpretative possibilities of EDMA data
A particularly significant anthropogenic activity linked with the clastic elements mentioned above is deforestation. An holistic approach to reconstructing palaeoenvironmental change is of considerable utility since it often places these allogenic signals in their wider geographical and temporal context. Figure 9.1 presents a model of environmental processes resulting from catchment deforestation and is discussed with reference to the results from three of the fieldsites which display signals linked to this activity. At Merrivale deforestation of the catchment between 395-140 BC is indicated by reduced levels of arboreal pollen, and increases for Poaceae and non-arboreal pollen. The introduction of mineral matter to the sediment system and the associated increased environmental acidity agrees well with the hypothesised model presented. However, at Piles Copse deforestation activity is recorded palynologically in the sediments from both PC1 and PC2, but there is no evidence for the resultant erosion of catchment mineral material, although at PC1 there is a progression to more acidic, anaerobic sedimentary conditions following the disturbance. These data suggest the scale of activity may have been sufficiently remote from the sedimentary system, explaining the absence of increased mineral matter. However, the more open nature of the catchment may have resulted in higher levels of runoff with an increased incidence of anoxic sedimentary conditions, particularly in the lower lying areas adjacent to the river channel. At Crift Down it is difficult to link the geochemical and palynological data with respect to deforestation activity since the former is dominated by high concentrations of mineral material throughout the profile. A tentative link does however exist. As the environment becomes more open so the level of mineral matter increases, although this may result solely from increasing industrial activities in the vicinity. The results from these fieldsites make it possible to suggest that geochemical data provide information of the nature of deforestation that has occurred. It seems that three different possibilities may arise following the detection of falling arboreal pollen values in the sedimentary record. The first relates to the loss of forest cover with no or little disturbance to the soil cover (e.g. Piles Copse); the second suggests loss of forest with erosion of soil material (e.g. Merrivale), and the third relates to the loss of forest with significant disturbance, including the erosion of basement material (e.g. Crift Down).

One of the more significant potential applications of geochemical studies of peatlands is the detection of heavy metal pollution from past anthropogenic activity (e.g. Livett et al., 1979; Livett, 1988; Van Geel et al., 1989; Stewart and Fergusson, 1994; Shotyk, 1996a,b). Increased levels of heavy metals have been detected globally from ice core repositories dating back to the fourth millennia BC.
Deforestation
- reduced arboreal pollen
- change in the pollen spectra - increase in ruderal species

 Soil disturbance and destabilisation

Erosion of catchment material
- increased levels of mineral matter (%ash)
- elevated Si, Al and other clastic elements, particularly on or near to granitic areas

Increased runoff

Increased waterlogging downslope
- enhanced leaching of poorly bound base elements (Na, K, Ca and Mg)
- production of sulphides (S, Cu)

Increased environmental acidity
- pH thresholds rapidly exceeded due to poorly buffered soils (reduced Al and base elements)
- enhanced production of sulphides (S, TOC and possibly Cu)
- sustained change in the pollen record, usually resulting in abundant representation of Poaceae species

PALAEOENVIRONMENTAL RECORD

Figure 9.1 A conceptual model of the record of deforestation activity as recorded in peatland sediments by geochemical and palynological indicators. Bold type indicates major processes with plain type suggesting main indications in the palaeoenvironmental record. These depend largely upon the location, magnitude of impact and the nature of the sedimentary system.
(Boutron, 1995) with dramatic increases for heavy metals, particularly Pb, attributable to the activities of the Roman era and later periods. This activity culminated in the widespread pollution of the global atmosphere which peaked during the 1970s (Grousset et al., 1994) due to the use of anthropogenic lead emitted from smelters and automobile exhausts (Martin et al., 1979; Hong et al., 1994; Renberg et al., 1994; Shotyk et al., 1996). It was expected to obtain similar results from analysis of the peatland sediments from south west England, as had previously been obtained from analysis of sites from widely differing geographical locations, detailing this increased heavy metal signature through time. It was also hoped, given the nature of the sediments chosen for analysis with associated archaeological remains indicative of intense tinworking activities, that the signals for prehistoric and Medieval exploitation would be recorded in the sediments. Neither of these have been generally possible using EDMA, again questioning its utility for the investigation of heavy metal pollution episodes from peatland sediments. Further discussion is made in section 9.2 and the results of some additional analyses are presented.

A further aspect of the environmental history of these sites relates to the possible evidence for climate change. Tor Royal is site most likely to contain signals relating to this process since the upper sediments are isolated from local soil water influences and are thus highly sensitive to changes in precipitation regime. A possible perturbation is recorded around the onset of Iron Age times in which increased levels of Sphagnum spores are linked with minor increases for Na and Ca, possibly derived from a change in regional atmospheric circulation.

**Autogenic group (Table 9.1)**

Sometimes the most dominant signals obtained from analysis of these sediments relate to processes operational within the sediment body as it accumulates through time. S is generally linked to TOC and as such relates to the production of sulphides in the anaerobic zone. Brown (1985) comments that 90% of the total S in valley mire peats is associated with organic matter and in a number of the areas investigated (Piles Copse and Crift Down) it seems likely that sulphides figure prominently in the geochemistry of the sediments.

Reconstruction of the palaeo-redox regime has been attempted for some time (Mackereth, 1966; Mannion, 1978). Indications from the sites investigated for this research suggest that the anaerobic/aerobic regime can sometimes be detected with respect to the presence of S and TOC indicating reducing conditions, with Fe suggesting precipitation of compounds under predominantly...
aerobic conditions (Tor Royal and Crift Down). The geochemical results also offer additional information with respect to the status and nature of sediment accumulation. At Tor Royal the basal sediments are characterised by groundwater circulation regimes with the transition to wholly ombrotrophic status reached at around 350 cm. Again, the different nature of sediment in the basal sediments from Crift Down is apparent with reference to the geochemical data. The basal *Salix* fen becomes progressively anaerobic with high levels of S, TOC and P, however the sediment immediately overlying this material (*Alnus* fen peat) displays signals characteristic of aerobic conditions.

The last group of signals belonging to the autogenic group are those associated with acrotelm processes, many of which were present in the sediments from the fieldsites investigated. The bio-accumulation of K was particularly noticeable and relates to the uptake of this nutrient in the modern living plant material (Shotyk, 1988; Alloway, 1995). Again the precipitation of Fe and Mn was sometimes noted in these upper layers of the sediment due to the aerobic status of the sedimentary environment at this time.

*Post-depositional diagenetic effects*

These are the most difficult processes to establish without compiling detailed geochemical inventories of modern inputs and outputs to the system. Much literature exists to suggest that base elements are most readily lost from peatland systems (Tanskanen, 1976; Damman, 1978; Shotyk, 1988), particularly where pore-water acidity is high due to the poor cation exchange capacity of these elements (Chapter 1). This seems to have been the case with Ca, K, Na and Mg, particularly where other geochemical assemblages suggest lower pH values to exist. The usefulness of these elements for palaeoenvironmental interpretations is limited, however it must also be stated that these elements are frequently associated with clastic materials, again stressing the importance to consider the assemblage of elements where diagenetic effects are suspected.

9.2 The accuracy of EDMA: comparative analyses using EMMA

It has already been stated that the EDMA results for the heavy metal elements are of questionable utility due to the detection limits of the analytical system and the influence of other elements. Further analyses were conducted using another geochemical technique to specifically address the accuracy of
Towards the end of the research the opportunity arose to carry out comparative analyses of sediment from Tor Royal and Crift Down using an Energy-dispersive Miniprobe Multielement Analyser - EMMA, (Cheburkin and Shotyk, 1996) as introduced briefly in section 1.3. This technique has been developed recently to provide multielement analysis of peat sediments for a range of elements, and is based upon an energy dispersive X-ray fluorescence instrument. The instrument benefits from the advantage of using considerably smaller samples than for conventional XRF analyses, with a larger beam size and a rotating sample stage included to reduce the problems of sample heterogeneity. The lowest limit of detection (LLD) for heavy metals (e.g. Pb, LLD=0.33μg/g) are approximately one order of magnitude lower than for standard XRF procedures. The advantages of EMMA in comparison to standard geochemical methods include the following: (i) no sample dissolution is required; (ii) several elements can be determined simultaneously, and; (iii) the EMMA technique is not generally subject to matrix interference.

Sub-samples of the original material analysed using EDMA were taken from 20 levels from the Tor Royal profile, with 22 samples taken from the Crift Down sediment. EMMA was capable of analysis of a limited range of elements, which for the Tor Royal sediment included Fe, Mn, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Pb and U, with the Crift Down analyses providing analytical data for the same elements with the exception of Ni and U, but with Y as an addition. The most significant use of this additional geochemical data is in the investigation of the accuracy and reliability of heavy metal determinations using EDMA, a question which occurred for every field site so far investigated with the exception of Sn from Medieval sediments (60-70 cm) at Crift Down, and the basal material from Piles Copse (PC1), with Pb detected in the lower samples from PC2. Unfortunately, EMMA was incapable of providing quantitative Sn concentrations (Andrij Cheburkin, pers. comm.), although further analyses of the Crift Down sediment using fusion ICP analysis with a detection limit of 1 ppm is a possibility (Eric Hoffman - ACTLABS, pers. comm.). The analytical error of EMMA results is ±15% for elemental concentrations lower than 20 ppm, and ±10% for all other concentrations.

The EMMA data thus has the possibility of providing comparative information on the EDMA results, but also provides a first approximation of detection limits for heavy metal elements using EDMA in sediments. The raw data are presented as elemental profiles (Figures 9.2 and 9.3), as well
as transformed data (Figures 9.4 and 9.5). The transformation was the same as carried out in Chapter 3, with the EMMA data standardised to 100% then transformed so that the mean values of each data set were the same, in this case zero. This allowed the direct comparison of profile features obtained by each of the analytical methods.

Iron and Manganese

The data are presented graphically on Fig. 9.2 and Fig 9.4 suggest a good deal of similarity between results obtained from EDMA and EMMA for Fe, examining both raw and transformed data sets. Raw data profiles exhibit very similar characteristics. Elevated concentrations in the basal section of the Tor Royal sediment decline over 2m but increase again towards the surface, with a very close correspondence exhibited for the transformed data, with generally small differences between the two plots. Similar characteristics are illustrated by both techniques for the Crift Down material with fluctuations in the lower metre of sediment and steadily increasing values from 60 cm to the surface. These data strengthen the reliability of Fe determinations using EDMA (cf. Chapter 3). However, Fe is usually considered a major component of peatland geochemical budgets, and given the way in which the EDMA technique produces data (as elemental percentages of analysed volume for the range of elements investigated, in this case fourteen), a major component will obviously be better represented than a more minor constituent. This is illustrated with reference to the Mn profile for both sites (Figs. 9.2 and 9.4). The concentration of Mn in the sediments from Tor Royal ranges from 10-112 ppm, and 16-162 ppm for Crift Down using the EMMA method. The percentage profiles produced by EDMA do not clearly replicate the concentration profile using EMMA, thus questioning the utility of EDMA for analysis of Mn. Similarly, the transformed data vary considerably with much deviation between the plots from each technique suggesting little correspondence between profile characteristics for the data. The transformed Mn plot from Tor Royal suggests a reasonable level of similarity, most likely due to the generally featureless nature of the EMMA Mn curve and the fact that both profiles display increasing elemental values above 100 cm. However, the transformed plot of Mn from Crift Down (Fig. 9.4) displays little relationship between the two profiles, and as such questions the validity of the Mn profile from this sediment. Manganese would be expected to behave in a comparable way to Fe in these environments, since it shares similar geochemical characteristics (Goldschmidt, 1954). This appears to be the case for the results from EMMA but not from EDMA (Fig. 9.2). These results are in general agreement with the data produced by AAS of the North Sands sediment (section 3.2, Figs. 3.4 and 3.6), in which there was
Figure 9.2 Comparative analysis of Fe and Mn using EDMA (solid line) and EMMA (broken line). EDMA results are given as a percentage of the element in the analysed volume (upper x-axis), with EMMA data presented in parts per million (ppm) on the lower x-axis.
Figure 9.3 Comparative analysis of Pb, As and Cu using EDMA (solid line) and EMMA (broken line). EDMA results are given as a percentage of the element in the analysed volume (upper x-axis), with EMMA data presented in parts per million (ppm) on the lower x-axis.
Figure 9.4 Comparison of Fe and Mn determinations using EDMA (solid line) and EMMA (broken line) data. Each data set is normalised to 100% then transformed so that the mean value of each set is the same (represented by vertical line). The plots therefore illustrate the comparability of results from each of the analytical methods.
Figure 9.5  Comparison of Pb, As and Cu determinations using EDMA (solid line) and EMMA (broken line) data. Each data set is normalised to 100% then transformed so that the mean value of each set is the same (represented by the vertical line). The plots therefore illustrate the comparability of results from each of the analytical methods.
generally good comparison between the AAS and EDMA Fe data, both raw and transformed, but little agreement between these two methods for Mn. Two possibilities therefore arise to explain this discrepancy:

(i) the levels of Mn present were below the LLD of EDMA, suggesting that the LLD of Mn from this type of sedimentary material was greater than 170 ppm.

(ii) EDMA was capable of detecting Mn from this sediment, but the data were obscured by the presence of more abundant elements in these levels e.g. Fe and Si. If this is the case then it identifies a fundamental flaw in the use of EDMA for trace elements.

Further discussion of the results obtained from analysis of As, Pb and Cu may provide some answers.

Heavy metal elements: Pb, As and Cu

The results are presented both as the raw elemental data (Fig. 9.3) and transformed data to allow independent comparison of profile characteristics (Fig. 9.5). The values for each element from both sites determined using EMMA and EDMA are given in Table 9.2 below, and illustrates possibly the LLD of EDMA with reference to the EMMA data.

<table>
<thead>
<tr>
<th>Element</th>
<th>Element range (ppm) by EMMA</th>
<th>Element range (% analysed volume) by EDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tor Royal</td>
<td>Crift Down</td>
</tr>
<tr>
<td>Pb</td>
<td>7-386</td>
<td>5-73</td>
</tr>
<tr>
<td>As</td>
<td>1-30</td>
<td>4-20</td>
</tr>
<tr>
<td>Cu</td>
<td>29-232</td>
<td>29-406</td>
</tr>
</tbody>
</table>

Table 9.2 Summary of heavy metal element ranges from Tor Royal and Crift Down

The data and elemental profiles suggest a general lack of correspondence between the results obtained by the two methods. A noticeable inter-correlation of the raw elemental profiles exists for Pb and As determined by EDMA from Tor Royal and in the lower section of the Crift Down sediment. This is a noticeable feature from virtually all of the sites so far investigated. With reference to the EMMA geochemical data the utility of EDMA for heavy metal analysis is questioned, and confirms the earlier fears with regard to the dubious results from EDMA for these elements.
The general lack of similarity for the heavy metal elements detected from Crift Down is illustrated with reference to both Fig. 9.3 and the transformed data, Fig. 9.5. The lack of correspondence between the EDMA and EMMA data for Pb, As and Cu is attributable to the problems of detection and masking seemingly inherent to the EDMA technique when dealing with these less abundant elements.

Another significant point to question the validity of heavy metal determinations using EDMA is the fact that the results are not interpretable in a meaningful manner, whilst those from EMMA reflect increasing anthropogenic activity and atmospheric metal deposition in these areas (West et al., in press) as stated earlier in the section.

The LLD for Pb and Cu by EDMA appear to be in the order of >400 ppm, which throws considerable question over the sensitivity of the technique to provide meaningful data relating to the changing concentrations of heavy metal elements from peatland sediments. The LLD for As appears lower (possibly >50 ppm). However, some useful information was obtained from EDMA of the Crift Down sediments which provided confirmatory evidence for Medieval tinworking in the locality. This suggests that the technique may provide interpretable information relating to heavy metal pollution in certain circumstances, however it is often the more subtle fluxes of these elements which is of interest to both the palaeoenvironmental scientist and environmental chemist alike.
Chapter 10

Conclusions and recommendations

10.0 Introduction

This chapter briefly provides a critical analysis of EDMA for use in palaeoenvironmental research based on the experiences of this project, with a brief section suggesting recommendations for the future of the technique in this sort of work.

10.1 Conclusions

The main findings of this research project may be summarised as follows:

1. EDMA has limited potential in the analysis of palaeoenvironmental investigations from peatland environments, due to a number of analytical problems identified previously which include detection limits and overall accuracy.

2. The results from EDMA may be used as a first approximation to the geochemical singatures of the sediment, but where specific elements are of interest more sophisticated techniques must be applied, particularly in the investigation of the less abundant trace and heavy metal elements.

3. Analyses of major elements (Si, Al, Fe) were the most reliable and compared well with results from comparative techniques. The association between these elements and mineral matter (ash%) indicated the major patterns of landscape degradation processes and instability, and were frequently associated with reduced levels of arboreal pollen.

4. Palynological investigation of the sediments was particularly fruitful and indicated the changing character of landscape at a variety of scales.
   - Analysis at Tor Royal served to illustrate in some detail the effects of prehistoric and historic activity upon central Dartmoor, the latter of which is particularly under-represented on the upland area.
   - Investigation at Merrivale suggests an intense but localised disturbance activity around the onset of Iron Age times, during which time the levels of trees in the catchment decline while grass pollen values expanded rapidly.
   - Similar results were obtained from analysis of two cores from Piles Copse. The results from site detected more recent deforestation activity (probably of 17th century AD date), confirming the suggestion of Roberts (1983) and others that the area known today as Piles Copse was planted around two hundred years ago.
- The results from pollen analysis at Crift Down confirm archaeological hypotheses for settled agricultural activity during Medieval times. It seems this activity intensified during the 14th and 15th centuries AD, and subsequently relates to a well developed arable and pastoral flora on the site.

10.2 Recommendations

Routine geochemical investigation of peatlands as part of a study of palaeoenvironmental conditions has much to offer in terms of the different environmental processes which were active both within the catchment as a whole, and within the accumulating sedimentary system. However, EDMA as a tool is generally incapable of revealing useful geochemical information due to various inherent analytical problems. This research suggests therefore that geochemical analysis of peatland sediments should be subordinate to palynology, and in particular EDMA should be used with great caution as a first stage investigative technique. However, the investigation of specific aspects in the geochemical history of a peatland site may be repaid by the application of other techniques, eg. AAS, XRF, ICP-MS based techniques, INAA, EMMA etc. These techniques have not been widely utilised in palaeoenvironmental studies, most have previously been concerned with the characterisation of metal pollution in modern day soils and plants (Johnson and Johnson, 1976; Jahnke et al., 1981; Hiraoka, 1994; Wilson et al., 1995; Dong, 1996; Goldstein et al., 1996; Pyle et al., 1996; Zbiral, 1996). There is limited evidence to suggest they are effective in the analysis of heavy metal elements from peatland sediments (Bengtsson and Enell, 1986). The use of some of these techniques also offers the possibility of isotopic analysis (ICP-MS) which may be specifically used to investigate the provenance of metals in peatland sediments (Shotyk et al., 1996).

Further work on different preparation techniques for EDMA, possibly involving finer grinding and pressing of material into discs may be fruitful and would possibly improve the quantitative accuracy of the technique, since it seems the analysis of ‘bulk’ samples hampered analytical operations. However, the additional work, and the effort required would be better employed in the analysis of the utility of other more sophisticated procedures for the characterisation of geochemical signals for palaeoenvironmental change.
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