RESEARCH REPORT
No. 77

Holocene lake sediment core sequences from Lochnagar, Cairngorm Mts., Scotland - UK Final Report for CHILL-10,000

Contract No: ENV4-CT97-0642

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Climate History as recorded by ecologically sensitive Arctic & Alpine Lakes in Europe during the last 10 000 years: A multi-proxy approach (CHILL-10 000), Contract No: ENV4-CT97-0642

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1. AIMS OF CHILL

The CHILL 10,000 project is funded under the EU Framework V, Environment and Climate Programme (Area 1.1.2). The aim of CHILL-10,000 is to quantitatively investigate past climate changes as recorded in lake deposits in ecologically sensitive situations. The biology of the systems (lakes) is used to amplify the climate signal. The objective in CHILL-10,000 is to undertake detailed, quality controlled and high resolution microfossil analyses of Holocene lake-sediment sequences. Biological proxy data include diatoms, chironomids, chrysophytes, pollen and cladoceran. Sedimentological proxy analysis including organic matter, minerogenic matter, mineral magnetism and particle size analysis are also conducted. The lake core sequences are dated using radiocarbon AMS dates of macrofossils or bulk samples of fine organic matter.

The CHILL project is co-ordinated by the University of Helsinki (Project co-ordinator: Dr. Atte Korhola) and project partners include the Institute of Limnology (Austria), University College London (UK), University of Edinburgh (Scotland, UK), University of Barcelona (Spain), University of Bern (Switzerland), Geological Survey of Denmark (Denmark), University of Bergen (Norway). Modern data-sets (or 'training sets') exist for three regions (the Alps, Pyrenees and Scandinavia) (Figure 1.1). Seven European lakes chosen for long-term climatic reconstructions (Redó D'aiqüestrotes (Spain), Sägistalsee (Switzerland), Unterer Landschitzee (Switzerland), Lochnagar (UK), Bjornfjellvatnet (Norway), Sjuodijaure (Sweden) and Masehjarvi (Finland) are also indicated in Figure 1.1. The sites are all close to modern timber line, with no glaciers in their catchments and have limited or no anthropogenic disturbance. The sites are generally all oligotrophic, small (< 20 ha), shallow (< 24 m) and clear (TOC < 5 mg l^{-1}).

1.1 Aims of CHILL at Lochnagar

The Cairngorm and Lochnagar mountain range constitutes the largest continuous area above 600 m, and is the only natural alpine environment, in the UK (Figure 1.2). The mountain ranges consists of a high tableland dissected by deep steep-sided glens. The geomorphology is ideal for collecting and holding snow. The massif is underlain by granite geology. The high altitude as well as harsh weather conditions have maintained infertile soils with a low carrying capacity.

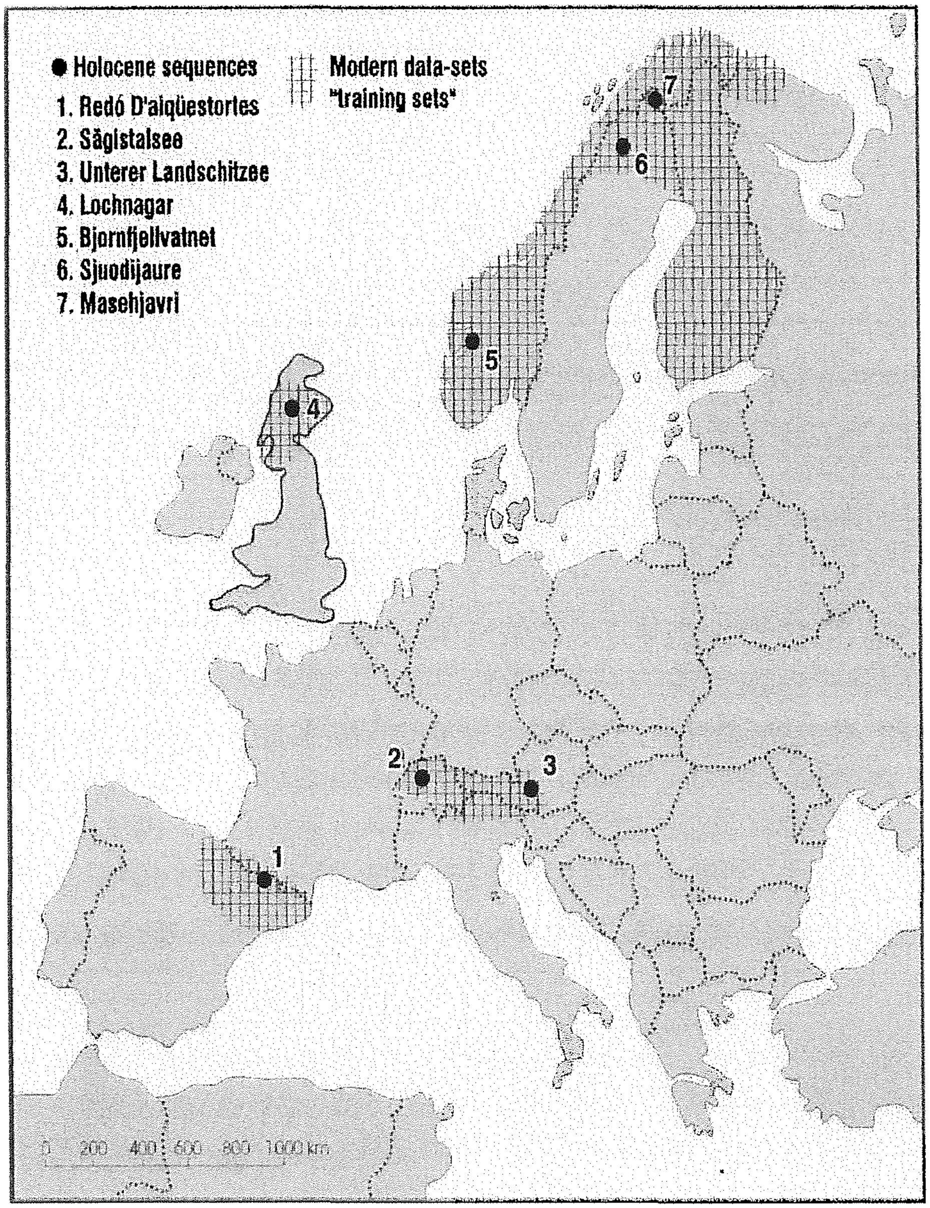


Figure 1.1: CHILL-10,000 training sets and lakes with Holocene sediment sequences

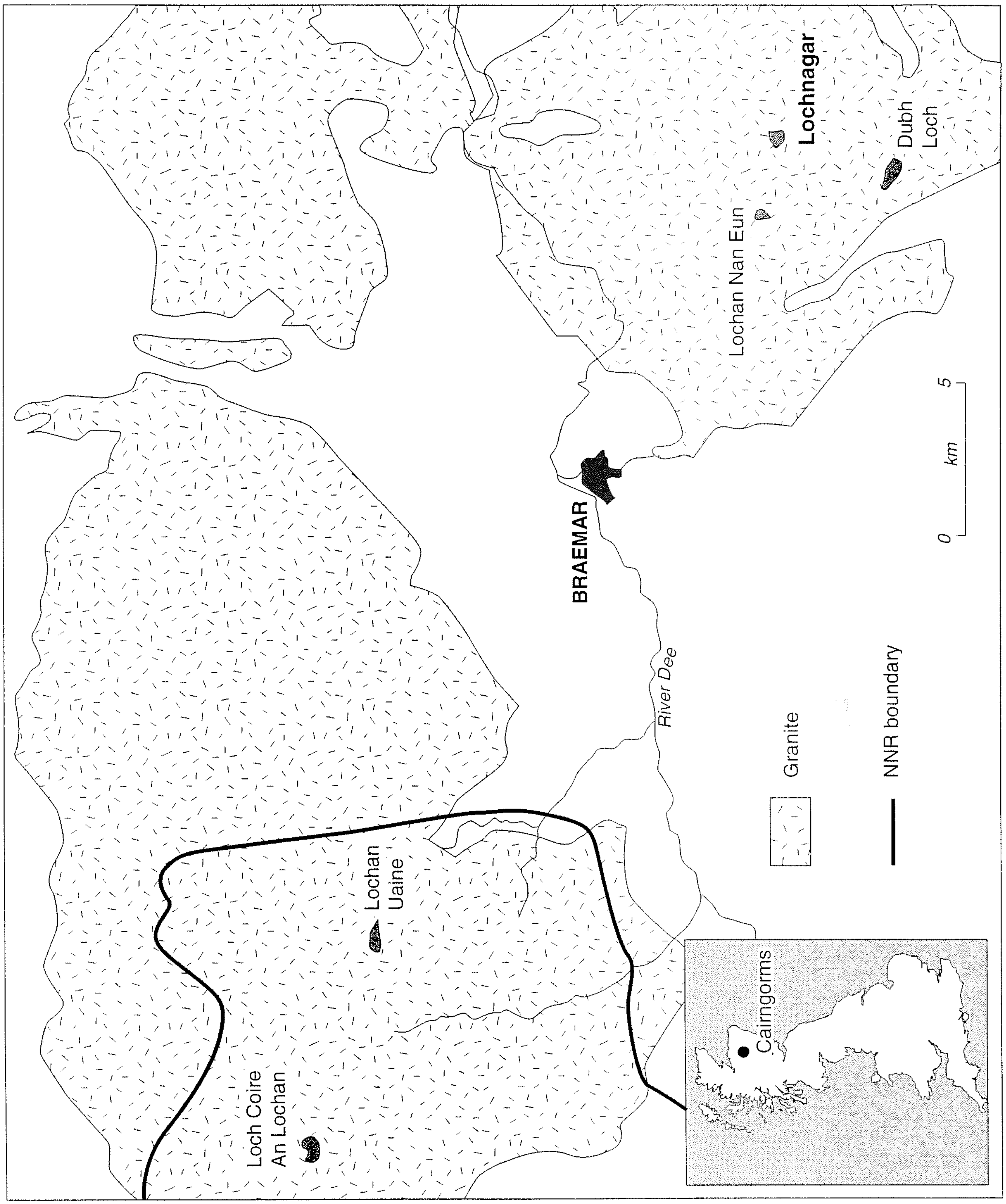
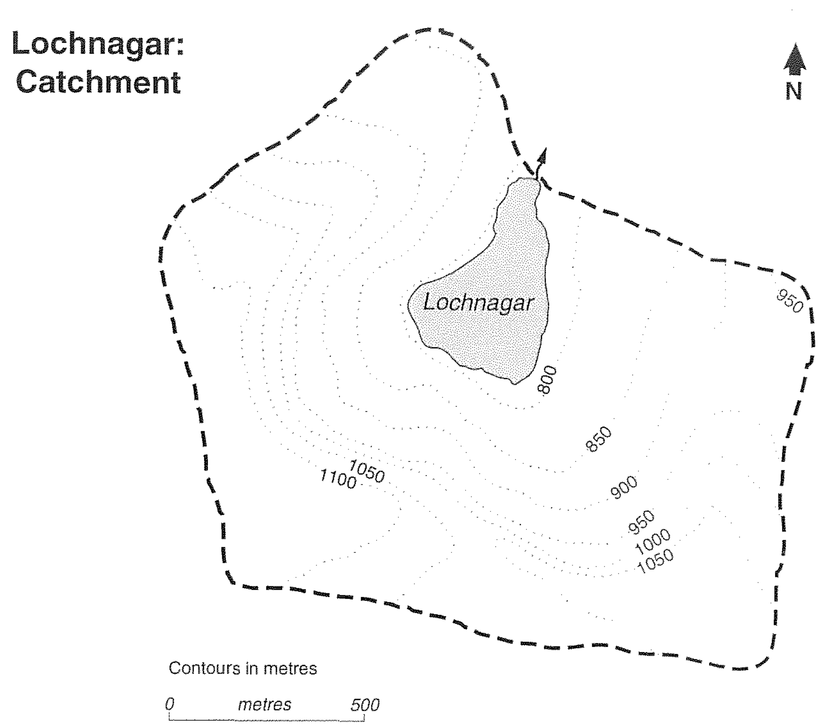


Figure 1.2: The Cairngorms and Lochnagar



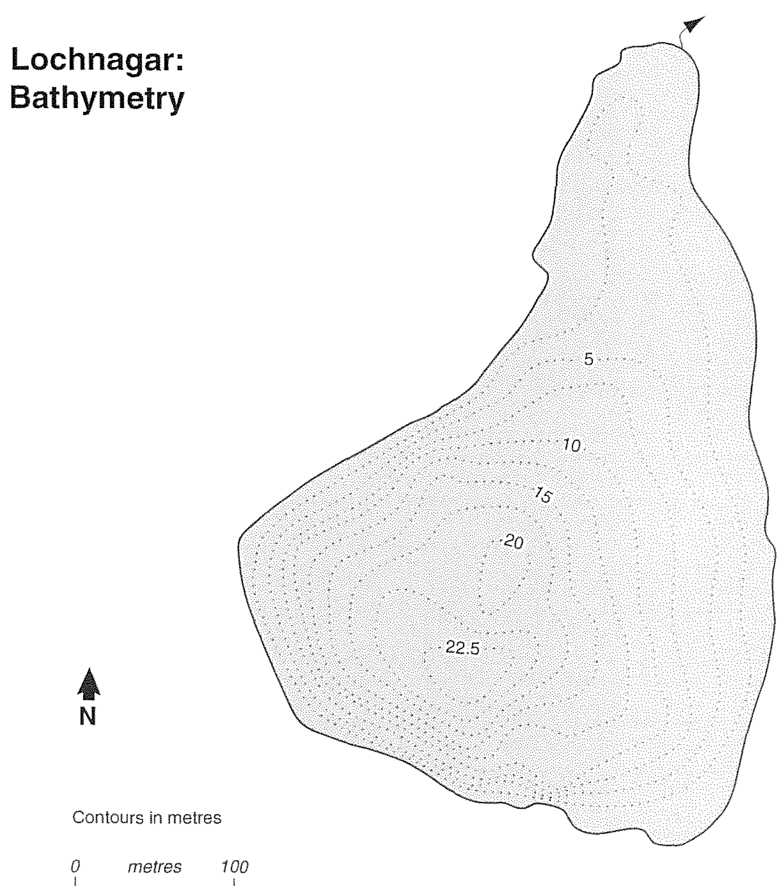


Figure 1.3: Lochnagar Catchment and Bathymetry

Lochnagar is one of the few lakes in Britain which is suitable for this study (Figure 1.2). It has a catchment in a high altitude situation where it is susceptible to the effects of climate change and is relatively undisturbed by human activity (Figure 1.3). In addition Lochnagar is the only high altitude corrie loch for which high quality monitoring data is available.

In collaboration with existing scientific work at Lochnagar, it was planned to retrieve a lake core with a Holocene sediment record. It was anticipated that the maximum depth of sediment accumulation, representing the last 10,000 years, would be contained within about 2.0 m of lake mud. The sedimentological and biological proxy data examined at Lochnagar are similar to the other CHILL lakes. In addition lake sediment geochemistry, biomarker and tephra studies are also being conducted at the UK site.

1.2 Research Objectives

The CHILL 10,000 research objective at Lochnagar is to examine proxy data for temperature and climate conditions. Changes in lake sediment stratigraphical data can be used to reconstruct past conditions. These proxies include organic and minerogenic matter as a bulk proxy for catchment and within-lake productivity, chironomids as a proxy for air temperature, diatoms as an indicator for lake water pH, pollen as an indicator of catchment vegetation and finally biomarkers to help determine changes in proportions of organic source material within the lake mud.

All CHILL partners will use sedimentological approaches (organic and minerogenic matter) as indicators of catchment and climate change. It appears that the relative proportions of mineral and organic matter can fluctuate in a cyclical manner and is possibly related to climate (Barber *et al.*, 1999).

Pollen analysis is being used to extend the existing pollen-climate training set for Scandinavia, the Alps and the Pyrenees. All CHILL partners will also study the pollen stratigraphy from Holocene lake sediment sequences in these ecologically and climatically sensitive situations.

The research objective for diatoms in the wider CHILL project is to extend and amalgamate the existing modern diatom-climate training sets in the northern Fennoscandia, Pyrenees, Switzerland, Austria and northern Italy that can then be used for climatic reconstructions from diatom-core data at ecologically sensitive high-altitude settings. There is no existing diatom-climate training set for the UK because of the low number of high altitude lakes unaffected by human impact. In addition diatom-temperature inferences have been criticised on the basis that they lack an ecophysiological basis, unlike diatom-based pH, salinity and nutrient reconstruction. Because of these limitations, the UK partner at Lochnagar will use the AL:PE diatom-pH training-set (Cameron *et al.*, 1999) to reconstruct historical pH as an appropriate alternative. Inferences about climate change will be interpreted via the lake water pH reconstruction and other paleolimnological proxies.

The research objective for chironomids is to expand the chironomid-water temperature training set for European alpine and arctic lakes and to use the modelled response functions to reconstruct past climates from the chironomid data. All partners will examine Holocene fossil records.

Changes in primary productivity are likely to be forced by climatic fluctuations and changes in the duration of ice cover. Organic biomarker techniques are used to explore the sources of mineral (clastic/diatom) and organic (algal/higher plant) fractions and the relative importance of lake and catchment material. Within CHILL biomarkers are used, by the UK partner at Lochnagar only, to develop the use of the technique for lake sediments as a means of identifying sources of organic matter. It is envisaged that this will assist in the investigation of the taphonomy of mountain lake sediments and enable a better understanding of radiocarbon dates and explore their potential as a proxy for climate.

Tephrachronology is also being conducted by the UK partner at Lochnagar to develop the technique for lake sediments. Lake sediment tephra have been counted from two profiles from Lochan Uaine, also in the Cairngorm region, however, shard concentrations were too low at this site for positive peak identification. It is envisaged that the higher concentration of organic matter in the sediments at Lochnagar will facilitate extraction of a better tephra shard record. This will in turn act as a potentially more precise dating horizon to support the inferred change from high resolution sediment analysis.

Surface sediment cladoceran analysis and chrysophyte analysis are being conducted at other CHILL sites to expand existing training sets and harmonise taxa. Holocene sequences are also being analysed for cladocerans and chrysophytes.

2. SITE SELECTION

Within the Cairngorm and Lochnagar ranges two sites were suitable for the CHILL project. The first Lochnagar, an AL:PE (Wathne *et al.*, 1995; Cameron *et al.*, 1999) & MOLAR (Patrick, 1997) site. The other site was Lochan Uaine a TIGGER site (Barber *et al.*, 1999). A Lochan Uaine sediment core was already available, however it did not cover the full Holocene sequence. This core consisted of a 95 cm sediment sequence covering *ca.* 5000 years. Problems with dating (a miss-match between extrapolated radiocarbon dates and ^{210}Pb) also made this site unsuitable. More cores from Lochan Uaine are currently being analysed by Andrew McGovern for his PhD at UCL. This work concentrates on organic geochemistry.

It was proposed to seek a full Holocene sequence from Lochnagar. A complete Holocene sediment record was thought potentially retrievable from Lochnagar as a result of previous work on Holocene sediments at this site (Rapson, 1985) and because of comparable sediment accumulation rates at upland Scottish lakes. The remoteness of the site meant that accessibility with long-coring equipment was problematic. Livingstone and Mackereth coring options were considered but the equipment was too heavy to carry to the site on foot and would have necessitated either helicopter or vehicular access. This equipment is also thought to cause major disturbance to surface sediments. An alternative was to develop a rope-operated piston corer, which would not require rods to operate and would be more portable for transport to this remote site.

Table 2.1: Location and environmental characteristics of Lochnagar

Site	Lochnagar
Latitude (°N)	59.95
Longitude (°E)	3.3
Altitude (m a.s.l.)	783
Lake area (ha)	9.8
Catchment area (ha)	91.9
Maximum depth (m)	24
July water temperature (°C)	11.2
July air temperature (°C)	12.4
pH	5.4
Conductivity (µS/cm)	21.5
Ca (mg l^{-1})	0.6
DOC (mg l^{-1})	1.0

A track and footpath facilitate physical access to Lochnagar. The lake is located approximately 2.5 hours walk from the car park at Glen Muick. The lake is located at an altitude of 783 m while Nagar the highest point in the catchment is at 1182 m (Table 2.1). The catchment area is 9.19 ha and lake area is 9.8 ha. An average pH for the lakewater is 5.4 and clear waters are evident with low mean DOC of 1.0 mg l^{-1}.

2.1 Sediment Coring

A tapper corer (for compact sediments) was designed by Jim Chambers and Nigel Cameron (Chambers & Cameron, in press) at the Environmental Change Research Centre, UCL. The tapper corer is a modification of existing percussion and piston-corer designs which can be used from small boats on open water. The device collects enough material for fine-resolution analyses. The core tube is hammered (with weights suspended from a second rope) beyond a piston secured by a rope and holding the core tube in place by friction. Retrieval of the sediment water interface is achieved by suspension of the piston approximately 30-50 cm above the sediment. Upon completion of the drive into the sediment (or when the core tube bottoms out) a lifting-pot is attached and the core tube with sediment and piston are retrieved.

Fieldwork was conducted at Lochnagar between July 14-17th 1998. Two long cores were obtained from the lake (NAG27 and NAG28). It was necessary to take two cores to have enough material for all analyses to fulfil the CHILL objectives. NAG27 and NAG28 were retrieved close to the deepest point in 20.4 and 20.6 m of water (Table 2.2). The cores measured 181.5 and 174.5 cm in length. Extrusion of the cores resulted in some compaction of the sediment and the final core lengths were approximately 176 cm (NAG27) and 171 cm (NAG28). The cores, taken 2 m apart (see Figure 2.1), appear to have very similar sediment accumulation rates with obvious matching colour changes offset by about 5 cm (also the difference in overall core length). The piston reached the head of the core tube and therefore the base of the potential sediment record was not retrieved.

A second fieldtrip was conducted between September 27-29th 1999 when a further two cores (NAG29 and NAG30) were collected. These were collected in an effort to extend the sequence to earlier Holocene sediments. These cores were retrieved from shallower lake perimeter waters (4.2 m depth). NAG30 measured 155 cm after core extrusion and was processed under the CHILL project. NAG29 is being analysed for heavy metals by Handong Yang at UCL. The retrieval of NAG30 from the littoral lake area was based on evidence of older sediments from previous coring work at this site (Rapson, 1985). The retrieval of a littoral core, with a different sedimentation regime, complicates interpretation of the sediment chronology. However, the

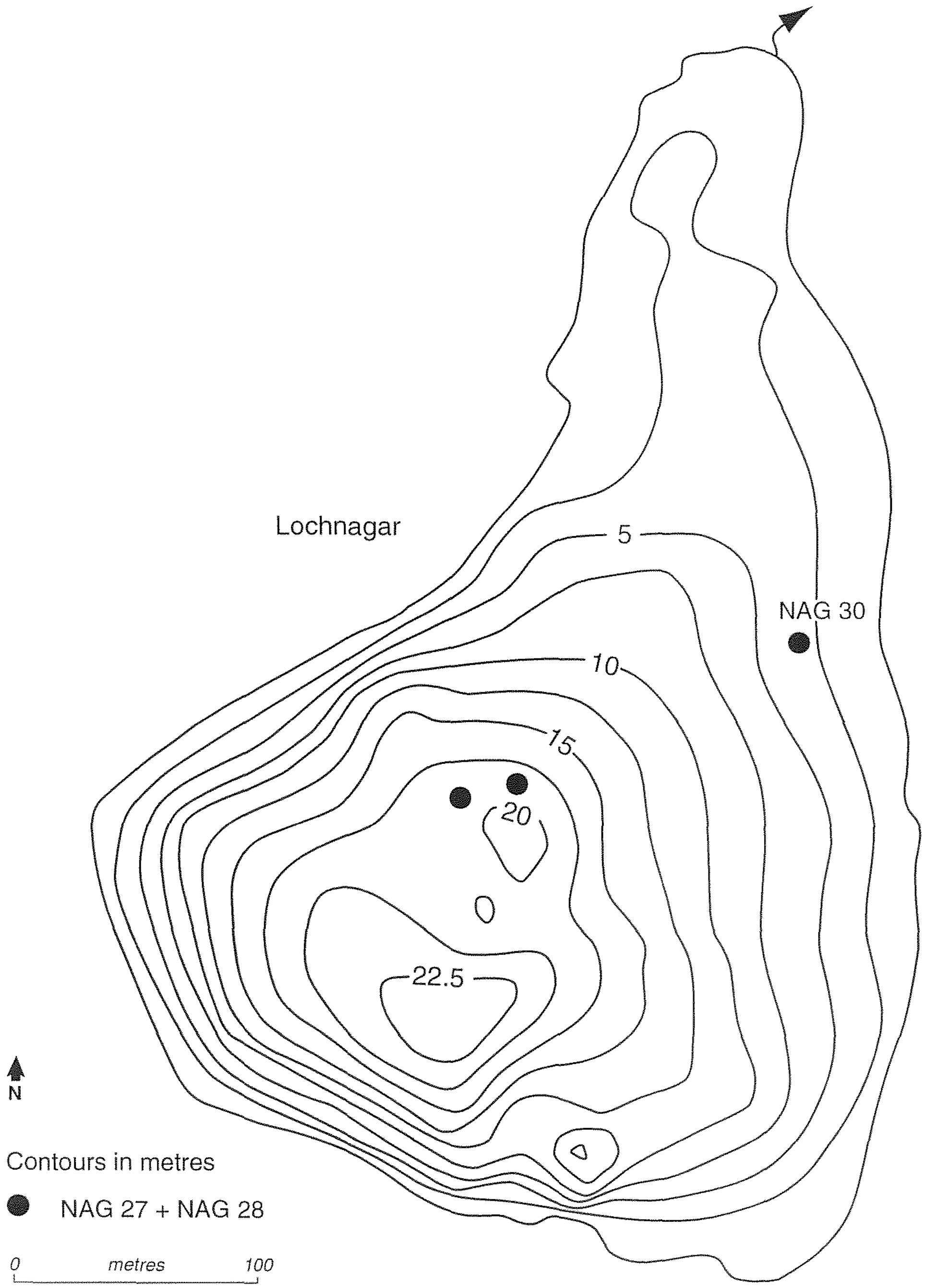


Figure 2.1: Lake bathymetry of Lochnagar and coring positions

overall aim to obtain a Holocene sediment sequence was achieved with the retrieval of deepwater and littoral sediment cores. To clarify interpretation from this point on NAG27 will be referred to as the master core as the majority of the sediment analysis was conducted on this core. Both NAG27 and the parallel core NAG28 are also referred to as the deepwater cores. NAG30 will be referred to as the littoral core.

Table 2.2: Lake sediment core details from Lochnagar.

Core Code	Date Cored	Water Depth (m)	Length of Core (cm)	Length of Core after extrusion (cm)
NAG27 (deepwater)	July 16, 1998	20.4	181.5	176.0
NAG28 (deepwater)	July 16, 1998	20.6	174.5	171.0
NAG29 (littoral)	Sept 29, 1999	4.4	170.0	167.0
NAG30 (littoral)	Sept 29, 1999	4.2	158.0	155.0

2.2 Sample Resolution

Sampling at fine intervals is necessary to achieve good resolution for detailed climatic reconstructions. The original CHILL proposal was for *ca.* 100 year resolution in contiguous sequences, however, use of finer time-intervals was optional. The Lochnagar cores were sliced at ultrafine intervals of 2 mm to enable fine-resolution examination of periods of environmental change of potential significance.

Core extrusion was limited by a suitable laboratory space and was eventually conducted vertically in a stairwell. Some contamination (smearing) of samples may have occurred from the actual coring as the tube passes down over the sediment and/or from the extrusion when the sediment is forced upwards through the tube. The main effort was made to extrude the core into sample bags and so make the cores safe as soon as possible. The 7.4 cm diameter deepwater cores (NAG27 & NAG28) were sliced at 2 mm intervals resulting in wet sediment samples of between 5-7 g. Efforts were made during sub-sampling to remove the outer ring (1-2 mm) of smeared sediment, to limit sample contamination. Extrusion (with two people) at 2 mm took 10 days for NAG27 and NAG28. The littoral core NAG30 was sliced at 1 cm intervals and took one day. In addition to scientific consideration sample intervals were determined by the amount of money available within the CHILL budget. Sample resolution was determined by the amount of material required for the particular proxy and the best representation across the core (Table 2.3). A total of 1,262 samples at 2 mm resolution were available from NAG27 and NAG28 while 154 samples at 1 cm resolution were available from NAG30.

Table 2.3: Lochnagar Sediment core sub-sampling - no. of samples and sample resolution in brackets

	NAG27 (deepwater core)	NAG28 (deepwater core)	NAG30 (littoral core)
DW & LOI	886 (2 mm)	376 (1 cm)	154 (1 cm)
Wet Density	27 (5-10 cm)		
Pollen	89 (6 mm)		41 (2 cm)
Chironomids		48 (8 cm)	19 (1 cm)
Magnetics & Particle Size		85 (2 mm)	75 (1 cm)
Organic Geochemistry (isotopes)		367 (2 mm)	
Biomarkers		35 (6 mm)	40 (2 cm)
Diatoms	184 (2 mm)		60 (1 cm)
Tephra Analysis	176 (1 cm)		64 (1 cm)

3. METHODOLOGY

3.1 Sediment Lithology

Munsell Colour

Attempts at Munsell colour classification were hampered by poor light conditions during sediment extrusion. The colour and textual changes were not marked in NAG27 and NAG28 however, the sediment was very fibrous from 30-35 cm. Some lighter colours were apparent around 70 cm, and 90 cm and 156 cm and a 2 cm mineral layer was found at 84 cm. No description of NAG30 was taken.

Wet Density (WD g cm^3)

The density of the wet sediment is measured using a 2 cm^3 capacity brass phial and a balance weighed to 4 decimal places. The clean phial is weighed empty and then carefully filled with wet sediment. Any air bubbles are removed by tapping the base of the phial on a firm surface and the surface of the sediment is then smoothed to be level with the top edge of the phial. The phial is then re-weighed and the weight of the sediment divided by 2 to determine the density as grams per cm^3. Wet density measurements were made every 5 cm to 90 cm and on every 10 cm to the base of the core (Table 2.3) due to limited changes.

Percentage Dry Weight (% DW)

Approximately 1 g of wet sediment was placed in clean, dry porcelain crucibles and balance weighed to at least 4 decimal places. The crucible was then placed in the oven for at least 12 hours set to 105°C. Following removal from the oven the samples were allowed to cool in a desiccator (to prevent re-absorption of moisture) before re-weighing. The percentage weight remaining after drying was then calculated. The same sample was then used for loss on ignition analysis. All samples were analysed from NAG27 (2 mm resolution), every 5th sample from NAG28 and every sample from NAG30 (1 cm resolution) (Table 2.3).

Percentage Loss on Ignition (% LOI)

The percentage weight lost on ignition gives a crude measure of the organic content of the sediment. Generally, percentage loss on ignition values show an inverse relationship with percentage dry weight values. The dried sediment samples in crucibles were placed in the furnace and kept at 550°C for 2 hours. Following removal from the furnace, samples were placed in a desiccator and allowed to cool fully before re-weighing. The percentage of the dry weight lost on ignition is then calculated.

UCL participated in an analytical quality control experiment to see how different laboratories within the CHILL project performed % LOI analyses (Heiri *et al.*, in press). The aim was to investigate whether the analyses on the same sediment are comparable between laboratories or only in the laboratory that did the analyses. The experiment was conducted on 20 pre-weighed sediment samples combusted at 550°C and 950°C. The results of this study suggest that within laboratory variation was small and that there is a laboratory specific pattern in the results. A 2% error was also found even when the standardised method was being used suggesting differences in laboratory equipment and/or handling.

3.1.1 Core Correlation

Dry weight and loss on ignition was conducted on all samples from the master core NAG27 (2 mm interval, 886 samples) and on samples at 1 cm and 2 mm intervals from NAG28 (376 samples). These two deepwater cores were subsequently correlated using a slot sequencing program (Clarke & Thompson, 1984). In sequence slotting the aim is to calculate the relative deposition rates in the two cores and to generate a diagram showing the tie lines. Figure 3.1 shows the correlated cores and their tie lines using dry weights and Figure 3.2 using loss on ignition. Because of the difference in sampling intervals between the cores the match at the top of the core was constrained. Core integrity, however, was not problematic. The cores are offset by a maximum of 9 cm according to the tie bars.

Core correlation between the deepwater cores (NAG27 and NAG28) and the littoral core (NAG30) was not attempted given the expected differences in the sedimentation regimes in distinct parts of the lake. Some chronological association between these profiles was initially estimated using pollen analysis and was later elucidated using calibrated radiocarbon dates.

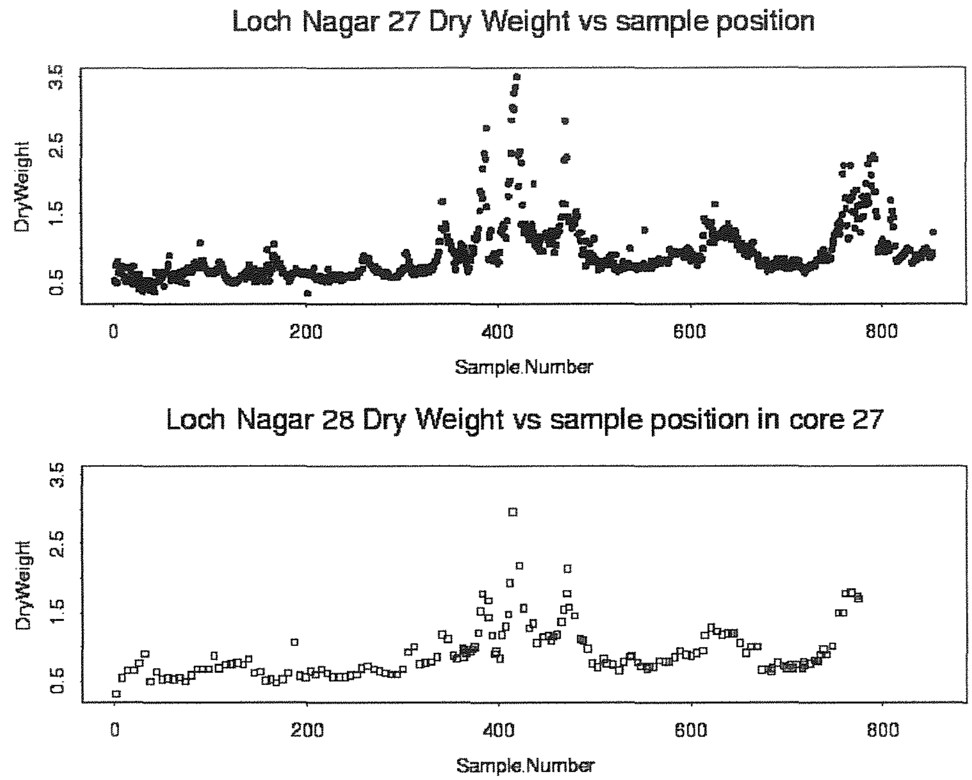


Figure 3.1: NAG27 & NAG28 %DW measurements correlated using tie lines

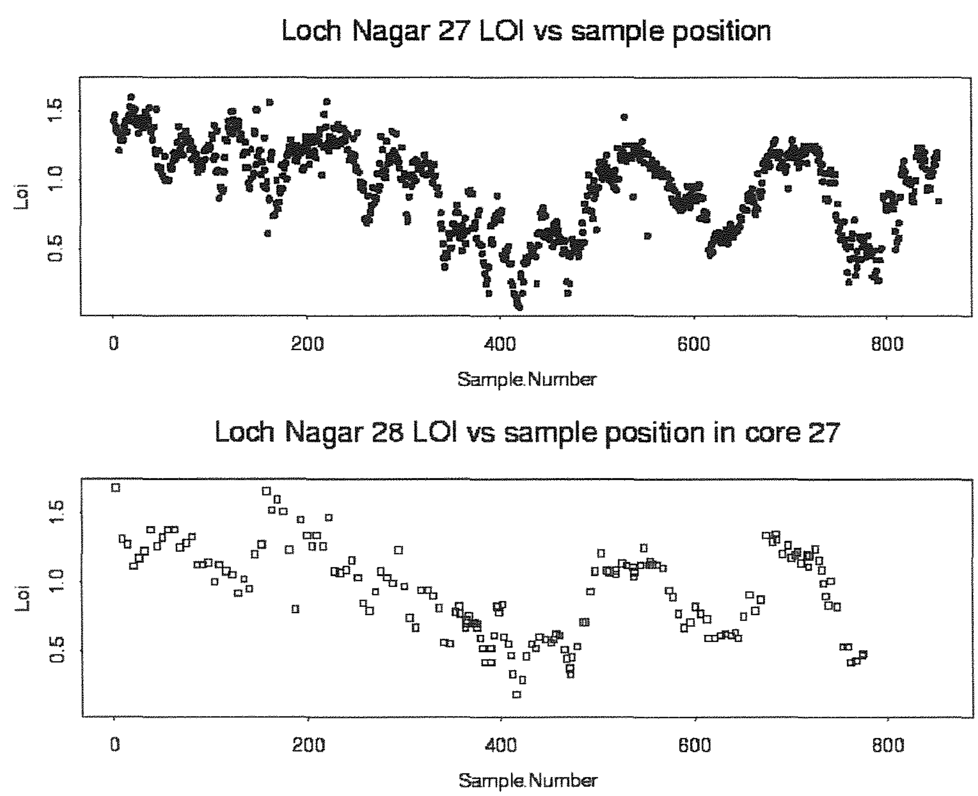


Figure 3.2: NAG27 & NAG28 % LOI measurements correlated using sequence slotting

3.2 Particle Size & Magnetism

3.2.1 Sample preparation

Sub-samples for particle size and magnetics were obtained at 2 cm intervals (2 mm resolution) from NAG28 (85 samples) and at 2 cm intervals (1 cm resolution) from NAG30 (75 samples).

For the magnetic measurements approximately 3.5 g of wet sediment was wrapped in clingfilm and firmly wedged into a non-magnetic perspex box. Following the magnetic measurements the samples were prepared for particle-size analysis and for the SEM work. Any carbonate was removed overnight in 20% acetic acid, then the sediment slurry centrifuged and washed three times. The organic component was digested using a 30% solution of hydrogen peroxide, which was heated in a water bath to 90 ^{o}C for one hour and left overnight. The following day the samples were again centrifuged and washed three times. The samples for particle-size work were stored in a solution of 4% sodium hexametaphosphate in order to disperse the clay fraction. Samples were stored for a maximum of two days and immediately prior to particle-size analysis, using a Coulter LS-100 laser diffractometer, were sonicated for 5 minutes. Samples for SEM analysis were diluted with distilled water following the removal of the carbonate and organic fractions, deposited on a metal stub and gold coated.

3.3 Organic Geochemistry

Samples for biomarker studies included 367 x 2 mm slices from the deepwater core NAG28 (171 cm core, 20.6 m water depth) and 40 x 2 cm samples from the littoral core NAG30 (155 cm, 4.2 m water depth). The samples were freeze-dried, crushed and passed through a 500 μm sieve.

Elemental Analyses

Quantitative carbon, nitrogen and carbonate measurements were performed twice on a 2 mm interval from each centimetre of the NAG28 core. The percentage reported values are the mean of two analyses. Total organic carbon (%TOC) content was calculated by subtracting the % carbonate value from measured % carbon.

Lipid extraction

0.5 g dry weight (DW) of three contiguous samples were bulked, to give samples of 1.5 g DW spanning 6 mm of core. A five-compound internal standard was added to each sample. Lipids were extracted by sequential sonication (10 mins) and centrifugation (10 min at 3000 rpm). Two extractions were carried out with 100% MeOH, two with 1:1 MeOH/DCM, one with 2:1 DCM/MeOH and two with 100% DCM. Solvents were removed by evaporation under vacuum, and the extract cleaned by passing through a short silica column with 2:1 DCM/Isopropanol. The lipid extract was separated into neutral and acid fractions with an aminopropyl Bond Elut column using 2:1 DCM/Isopropanol and 5-10% acetic acid in diethyl ether respectively. The neutral fraction was further fractionated into hydrocarbon, aromatic, ketone and wax ester, alcohol and sterol, and polar fractions by flash column chromatography (using the following sequence of solvents: hexane; 9:1 hexane/DCM; DCM; 1:1DCM/MeOH; MeOH).

GC-MS

The alcohol/sterol fraction was derivatised in BSTFA prior to GC-MS analyses. Hydrocarbon and alcohol/sterol fractions were run on a Varian 3400 gas chromatograph (70 eV EI, SPI type injector) with a direct interface to a Finnigan TSQ 700 mass spectrometer. A temperature programme of 40°C (1 min) - 200°C @ 10°C/min - 300°C (20 mins) @ 3°C/min was used for standard GC runs and helium was used as the carrier gas. Lipids were identified at first by mass spectral analysis, and thereafter by comparison of GC retention times under constant operating conditions.

Elemental Analyser - isotope ratio mass spectrometry (EA-IRMS)

On-line bulk $\delta^{13}C$ analyses of sediment were performed using a Fisons Carlo Erba NC2500 elemental analyser coupled to a Finnigan MAT Delta S instrument via a ConFlo2 interface. Analysis of each sample (*ca.* 3 mg in tin capsule) was carried out in duplicate to obtain a mean value and nonadecane was run frequently as a standard compound within batches of samples.

Plant and peat samples have been crushed and freeze-dried: these will be extracted to determine their lipid composition and contribution to the sedimentary organic matter. Comparing the carbon isotope ratios ($\delta^{13}C$) of individual *n*-alkanes from the plants with those from the lake sediments will help to discriminate between the sources of the sedimentary carbon.

Chlorins

Chlorins have been extracted with DCM/ acetone from 2 mm samples at 5 cm intervals along NAG28. These were quantified by UV/ visible spectrophotometry according to Jeffrey and Humphrey (1975).

3.4 Pollen

Volumetric samples (0.5 cm^2) were taken for pollen analysis using a quantitative sampler. Samples at 2 cm intervals from core NAG27 were obtained by amalgamating material from three consecutive 2 mm sediment slices. Samples from core NAG30 were taken directly from the 1 cm sediment slices. Samples were prepared for pollen analysis using a standard preparation protocol (procedure B in Berglund & Ralska-Jasiewiczowa, 1986) and the residues mounted in silicone oil (2000 cS). Pollen counting was performed at a x400 magnification (bright field), with critical determinations at x1000 magnification using an oil-immersion objective. About 600 grains and spores were counted in each sample.

All pollen and spores of non-obligate aquatic taxa are included in the calculation sum (SP) and expressed as percentages of SP. Pollen and spores of obligate aquatic taxa, algae, *Sphagnum*, indeterminable and unknown grains, and microscopic charcoal particles are expressed as percentages of SP + S relevant category (see Birks, 1973).

The pollen-stratigraphical data from cores NAG27 and NAG30 are plotted in Figures 4.16 and 4.17, along with the available radiocarbon dates, the pollen zonation, and the modelled calibrated age scale (cal yr BP) derived from the age-depth models for cores NAG27 and NAG30. All stratigraphical plots were drawn using the computer program TILIA-GRAPH written by E.C. Grimm.

Numerical analyses of the pollen-stratigraphical data were performed to answer the following questions. (1) Can the pollen stratigraphies from the two cores be correlated on the basis of pollen composition and how does this biostratigraphical correlation correspond to a chronological correlation based on the two age-depth models for cores NAG27 and NAG30? (2) What is the appropriate zonation for the total stratigraphy, given the likelihood that part of the NAG30 core overlaps with part of the NAG27 sequence? (3) What are the major underlying gradients of variation in the pollen-stratigraphical data?

All numerical analyses were based on taxa included in the calculation sum. The percentages were transformed to their square roots to stabilise variances and to maximise the 'signal to noise' ratio. As the total compositional change in the combined stratigraphy is 0.97 standard deviations (as estimated by a detrended canonical correspondence analysis constrained by sample order with detrending by segments, non-linear rescaling, and downweighting of rare taxa), the linear-based ordination technique of principal components analysis (PCA) and sequence-slotting (Birks & Gordon, 1985) were used to answer question (1). Optimal sum-of-squares partitioning (Birks & Gordon, 1985) and comparison with the broken-stick model to assess the approximate statistical significance of the zones (Bennett, 1996a) were used to answer question (2). PCA was used, in conjunction with the broken-stick approach, to answer question (3). Computations were implemented using the computer programs CANOCO version 3.12a with strict convergence criteria, CANODRAW, ZONE, SLOTSEQ, and BSTICK.

3.5 AMS ^{14}C Dating

Terrestrial plant macrofossils were considered ideal for AMS ^{14}C dating however few were present in the Lochnagar sediment samples (S. Peglar, pers. comm.). Bulk samples of fine organic material (particulate fraction) were considered the best alternative and adopted for the Lochnagar samples. AMS ^{14}C Dates were obtained from the Dating Laboratory, University of Helsinki, Finland. Lake sediment samples from Lochnagar were stored in polythene bags in a fridge at 4°C. Samples for dating were transferred to sterilised glass bottles. Pre-preparation of all CHILL samples for dating was conducted at the dating laboratory.

3.6 Diatoms

Diatom samples were prepared using known volumes of wet sediment placed in polyethylene test-tubes and digested in a waterbath using the standard hydrogen peroxide (H_2O_2) method (Battarbee, 1986). The mixture was boiled in a fume cupboard for approximately 2 hours or until all the organics were removed. After adding a few drops of HCl to remove the remaining H_2O_2 the mixture was then allowed to cool and settle. The samples were then washed clean with distilled water, centrifuged and the supernatant discarded. Prior to the last wash 1% NH_3 was added to disperse the diatoms and prevent clumping. This diatom solution was subsampled at a suitable concentration and the aliquot placed on a microscope coverslip (*ca.* 18 mm x 18 mm). The coverslips were placed on a metal plate and allowed to dry slowly (1-2 days). The dried samples were subsequently inverted and placed onto a drop of a mounting medium Naphrax on a microscope slide. The mount was then made permanent by evaporating the Naphrax solvent with a hotplate temperature of 130 °C.

To determine diatom concentrations (cells g wwt^{-1}) a known number of microscopic markers were added to a known amount of sediment (Battarbee & Keen, 1982). Divinylbenzene (DVB) spheres are added to the diatom suspension prior to slide preparation.

Diatom accumulation rates (valves cm^{-2} $year^{-1}$) can be calculated for sediments that have been dated (radiometrically). Diatom accumulation rates (valves cm^{-2} $year^{-1}$) were calculated by multiplying the wet mass accumulation rate (cm^{-2} $year^{-1}$) and the diatom concentration (cells g wet wt^{-1}).

Diatoms were prepared at 2 mm intervals from the master deepwater core NAG27 (886 samples) and have been counted at 1 cm interval (185 samples) to pick up temporal trends. Samples at 1 cm intervals were prepared and counted for the littoral core NAG30 (60 samples). Low sum diatom counting (*ca.* 100-200 valves) was conducted on all samples (Renberg, 1990).

Diatom counts were entered into the diatom database AMPHORA at University College London Data manipulation was performed using TRAN (Juggins, 1994) to create Cornell condensed format percentage data. TILIA and TILIAGRAPH (Grimm, 1991) and Microsoft EXCEL were used for storing, manipulating and plotting stratigraphic diatom data. Polynomial trendlines (order 6) were added to a number of EXCEL plots to aid interpretation. The diatom data were subjected to zonation and ordination techniques. Zonation of stratigraphical fossil diatom data was achieved using ZONE and BSTICK. ZONE uses a number of methods to analyse stratigraphic data (CONSLINK (using a Chord distance dissimilarity matrix), CONISS (using a Squared Chord distance dissimilarity matrix), SPLITLSQ, SPLITINF and Cluster analysis) and BROKEN STICK (Bennett, 1996) is used to determine if the zones are statistically significant. Principal components analysis (PCA) a linear ordination method was used to reflect the pattern of the species data in the ordination axes. Interpretation of the pattern or structure is based on the known ecological preferences of the species according to the literature.

3.7 Chironomids

Initially, samples at 4 cm intervals from core NAG28 were obtained by amalgamating material from four consecutive 2 mm sediment slices. Samples from core NAG30 were taken directly as 1 cm sediment slices at 5 cm intervals. Subsequently a few samples were taken at higher resolution in order to pin-point the position of zone boundaries in the chironomid stratigraphy.

Detrended correspondence analysis (DCA) was used to assess the species turn-over along the environmental gradients. The species data was square root transformed, with detrending by segments, non-linear rescaling and rare taxa down-weighted. Because the standard deviation of both DCA axes 1 and 2 was less than 2.0 this indicates a linear species response and so principal components analysis (PCA) was appropriate for further analysis of the data.

Using the computer programme CALIBRATE a 153-lake modern Norwegian chironomid-mean July air temperature calibration set (Brooks & Birks, unpublished) was used to reconstruct mean July air temperatures from the fossil chironomid assemblage of Lochnagar. The calibration set includes lakes covering a latitudinal gradient from Svalbard to southern Norway, a mean July air temperature range of 3.5°C-16.0°C, and an altitudinal range of 0-16,700 m a.s.l..

3.8 Tephra

Tephra shards were extracted from the Lochnagar lake sediments using H_2O_2 to remove organic matter, NaOH to remove biogenic silica and HCL to remove carbonates and bicarbonates, a procedure described by Rose *et al.*, (1996). Known amounts (*ca.* 0.1 g) of dried lake sediment are placed in glass test tubes and 2 ml of 30% H_2O_2 added. Cold over-night digestion is followed by the addition of 5 ml of H_2O_2 and digestion in a waterbath at 80°C for 3 hours. Samples are then allowed to cool centrifuged and the supernatant is discarded. Five ml of 0.3M NaOH is then added and heated in a waterbath for 3 hours. A final 5 ml of 3M HCL is then added and samples are digested in the waterbath for 1 hour. A known fraction of the final residue is evaporated on coverslips.

Tephra are counted under a light microscope with a rotating stage and cross polarised light. Shard concentrations are expressed in units of g DM^{-1}. All the shards present on the coverslip are counted.

4. RESULTS

4.1 Sediment Lithology

4.1.1 Loss on Ignition and Dry Weight - C.P. Dalton, University College London

The sediment lithology of Lochnagar is characterised by multiple peaks and troughs in organic matter and very sharp peaks in dry weight in the master core NAG27 (Figure 4.1). These variations are replicated in the results for the parallel deepwater sediment core NAG28 (Figure 4.2). NAG30, on the other hand, collected closer to the perimeter of the lake has a less variable profile with lower levels of organic matter (Figure 4.3). This could be related to the lower resolution analysis (1 cm intervals) being less sensitive to sediment change or may be a factor of spatial variation within the lake sediment body. However, lower sample resolution analysis of NAG28 (1 cm) did not reduce the signal compared to NAG27 (2 mm), so this could not account for the results in NAG30. A peripheral lake sediment core closer to catchment peats should potentially have higher levels of catchment derived organic matter, therefore, the lower %LOI values for NAG30 was unexpected. Sediment bulk or wet density measurements varied between 1.01 and 1.14 g cm^3 (on NAG27). Little overall change in bulk density is apparent.

The hypothesis is that peaks in loss on ignition represent phases of higher productivity at the site. The profiles for NAG27 and NAG28 may therefore represent oscillations in productivity over the 6200 calibrated year period covered by the sequence (see section 4.2). In the bottom half of the NAG27 core three major peaks and three toughs in organic matter are clearly identified. This corresponds to the period 6200-4000 cal yr BP. The major troughs coincide approximately with calibrated dates of 5800, 4800 and ~3500 cal yr BP. Periodicity's pre-3000 years, therefore, appear to be based on approximately 1000-year cycles.

Post-3000 cal yr BP there is a 3-4-fold increase in oscillations with approximately 10 peaks in organic matter. These periodicities of 250-350 years represent a major change in the Lochnagar system post-3000 cal yr BP.

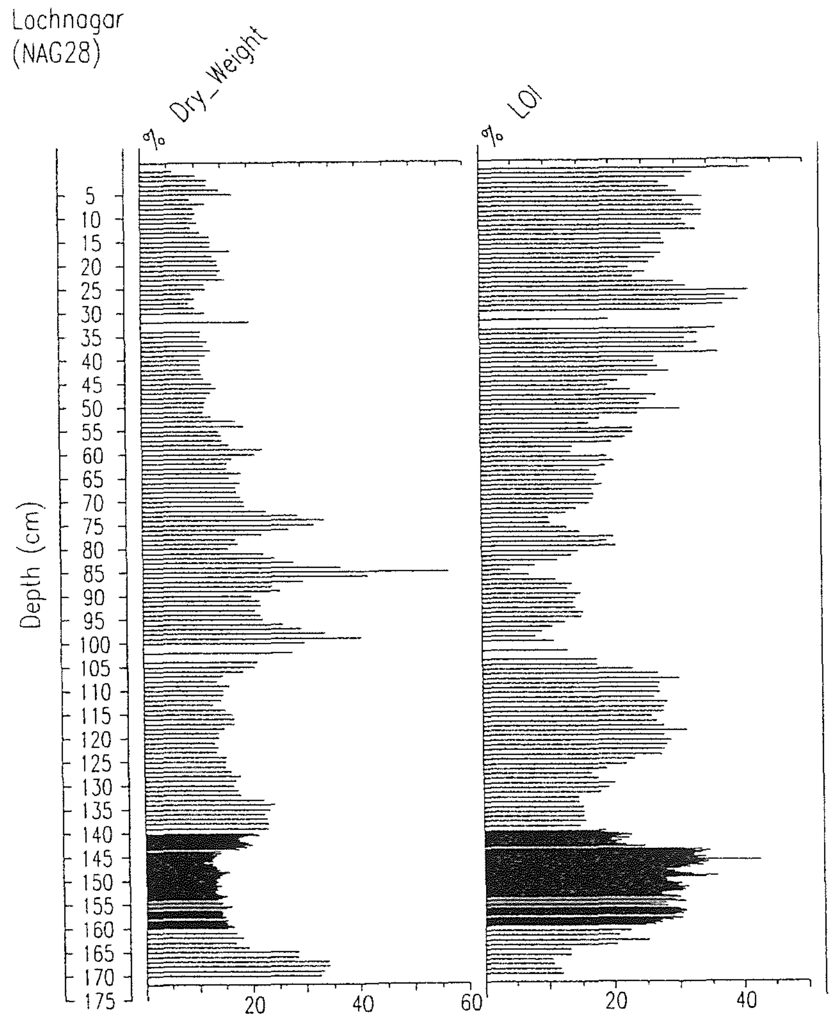


Figure 4.2: Lochnagar sediment lithology (NAG28), including dry matter (% dry weight) and organic matter (% LOI)

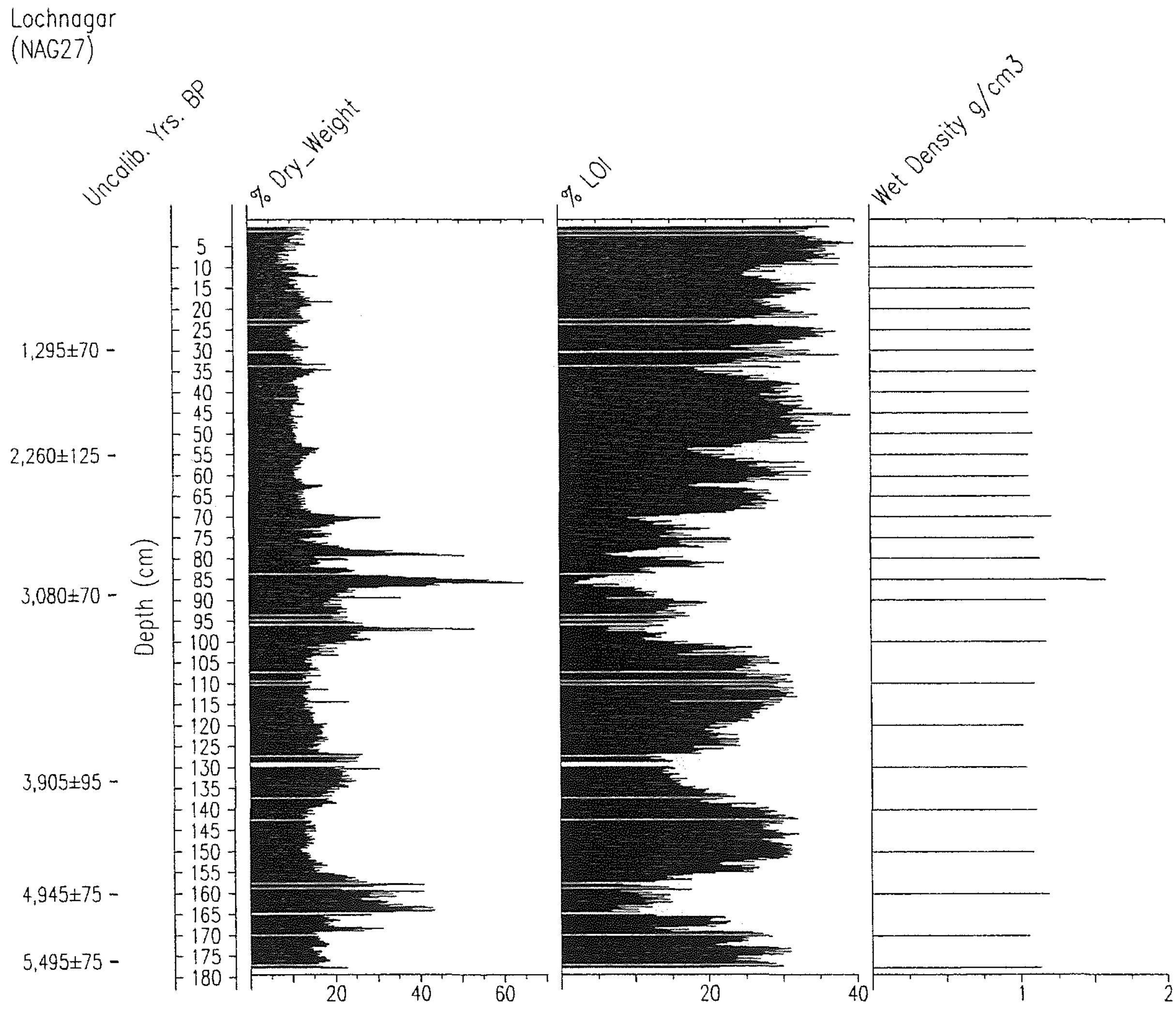


Figure 4.1: Lochnagar (NAG27) sediment lithology, including bulk density (wet density g m[3]), dry matter (% dry weight) and organic matter (% LOI)

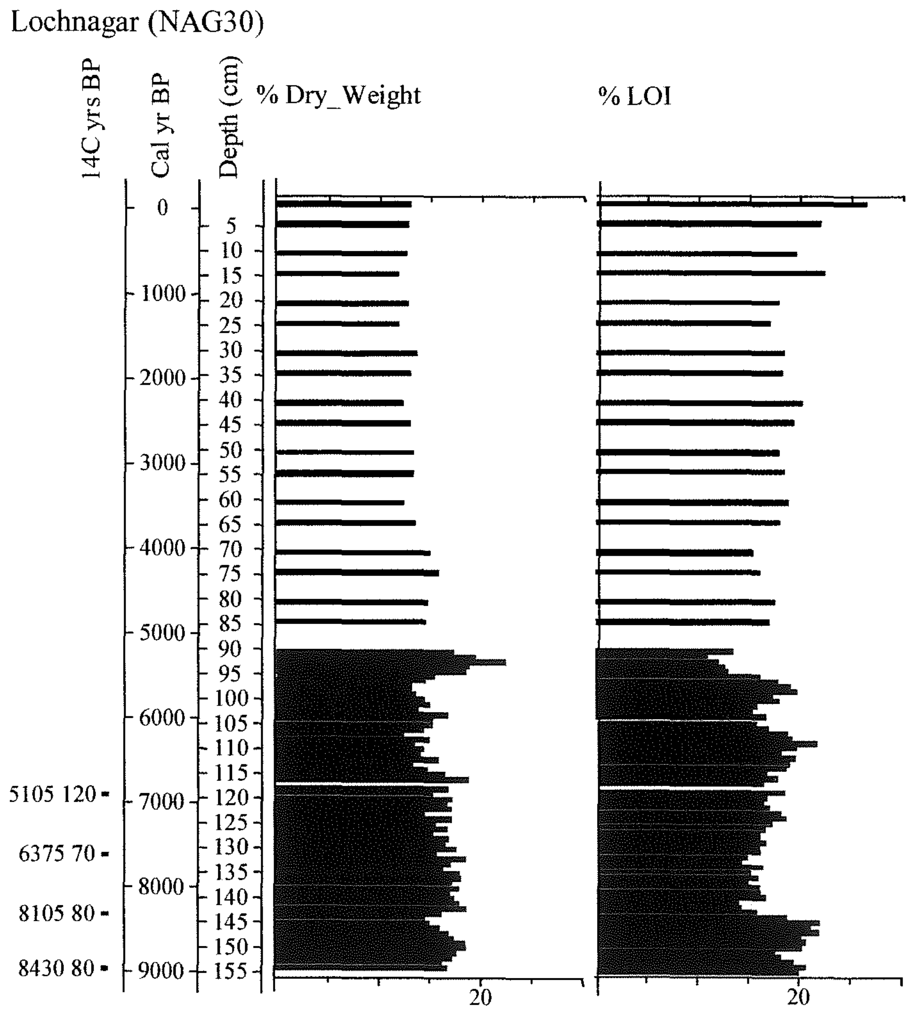


Figure 4.3: Lochnagar sediment lithology (NAG30), including dry matter (% dry weight) and organic matter (% LOI)

The sediment dry weight exhibits peaks and troughs in the profiles and generally shows an inverse relationship with loss on ignition measurements (Figures 4.1, 4.2 and 4.3). Dry matter rarely drops below 15% in the lower half of the core (pre- 3000 cal yr BP) and 10 % in the upper half, post-3000 cal yr BP in NAG27 and NAG28. Of note are three peaks in dry matter between 100-75 cm. Peaks of 50-65% dry weight are recorded for NAG27 and up to 60% for the parallel core NAG28. These correspond to major troughs in LOI. These high DW levels suggest a major catchment minerogenic input around 3000 cal yr BP and may represent the first effects of anthropogenic disturbance in the catchment. The dry weight profile for NAG30 from shallower water shows a more uniform record with maximum % DW levels of just 20% (Figure 4.3). A gradual decline in %DW and increase in % LOI is evident up the core.

4.1.2 Particle size and magnetism - R. Thompson & S. Derrick, University of Edinburgh

4.1.2.1 Introduction

Lake bottoms are the depositional site of both minerogenic and organic matter that is transported to the lake from the surrounding drainage basin as well of as matter that forms within the lake itself. Thus lake sediments typically consist of accumulates of minerogenic particles (e.g. quartz or feldspar), plant fragments, diatom frustules and calcium carbonate precipitates. Mountain lakes, with small inflowing streams, can often contain bottom sediments dominated by diatoms. Following removal of the organic fraction, particle-size analysis forms a quantitative approach to characterising the non-organic component of lake sediments. A previous study at Lochan Uaine, a high corrie loch in Scotland, revealed a relationship between particle-size and the key stratigraphic parameter of loss-on-ignition. The cause of the relationship however was not discovered. Three potential controls on the particle-size distribution in remote mountain lakes are (i) changes in the importance of catchment erosion, (ii) changes in the preservation (e.g. breakage) of diatom frustules and (iii) changes to the diatom flora. One hundred and sixty samples of bottom sediment from Lochnagar spanning approximately the last 9,000 years, have been analysed to further investigate the particle-size distribution of remote mountain lake sediments and the relationship of particle-size and magnetism with biological proxies of climate change.

4.1.2.2 Results

Particle-size

The sediments of Lochnagar predominantly consist of silt sized particles with smaller percentages of clay and sand. Uni-modal, bi-modal and even tri-modal particle-size distributions are found (Figure 4.4). The median sediment size is about 18 μm in diameter for both the littoral and deepwater sediments. The middle section of core NAG28 contains significantly sandier horizons (Figure 4.5).

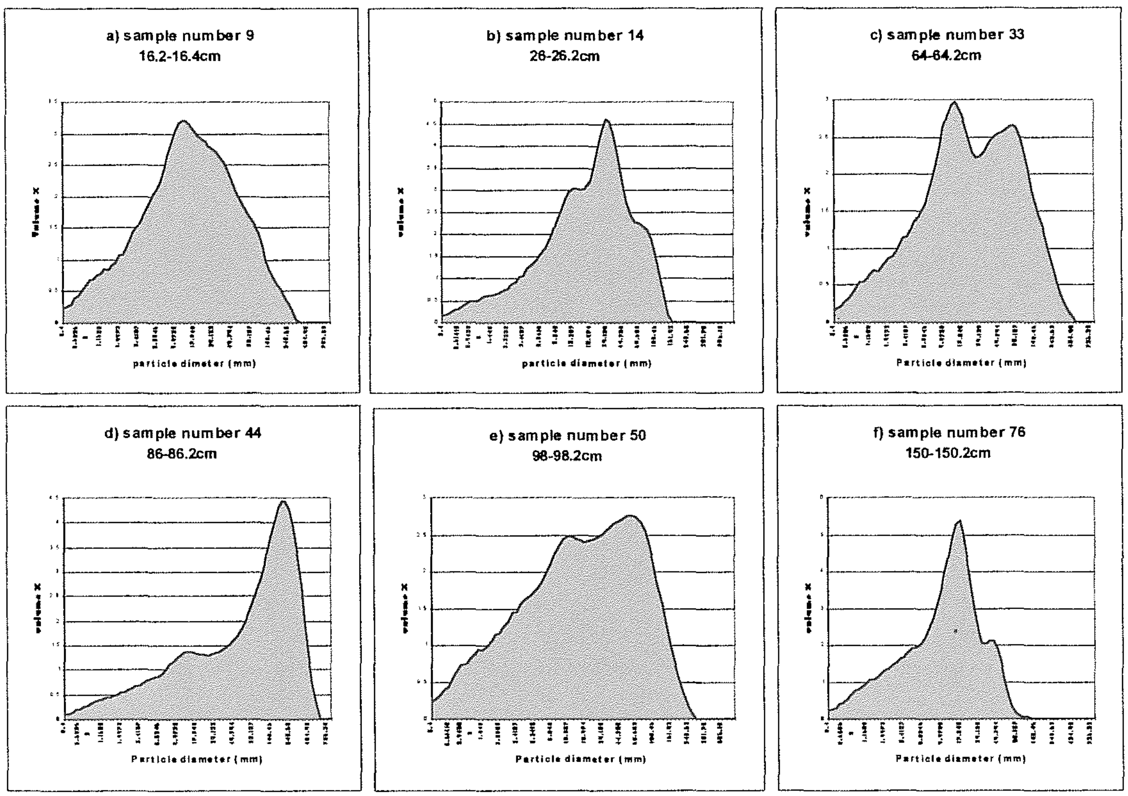


Figure 4.4: Particle-size distributions for six horizons in Lochnagar (NAG28)

Magnetism

The magnetic properties of Lochnagar sediments are very weak, nevertheless a cryogenic magnetometer can, with care, be used for their measurement. The sediment typically only contains about one grain in one hundred thousand, which is magnetic. Magnetic concentration varies with sediment age. The highest magnetic concentrations are found in the sediments near the top of the core sequences (Figure 4.6). Concentrations for the littoral core NAG30 are an order of magnitude lower than those of the deepwater core NAG28.

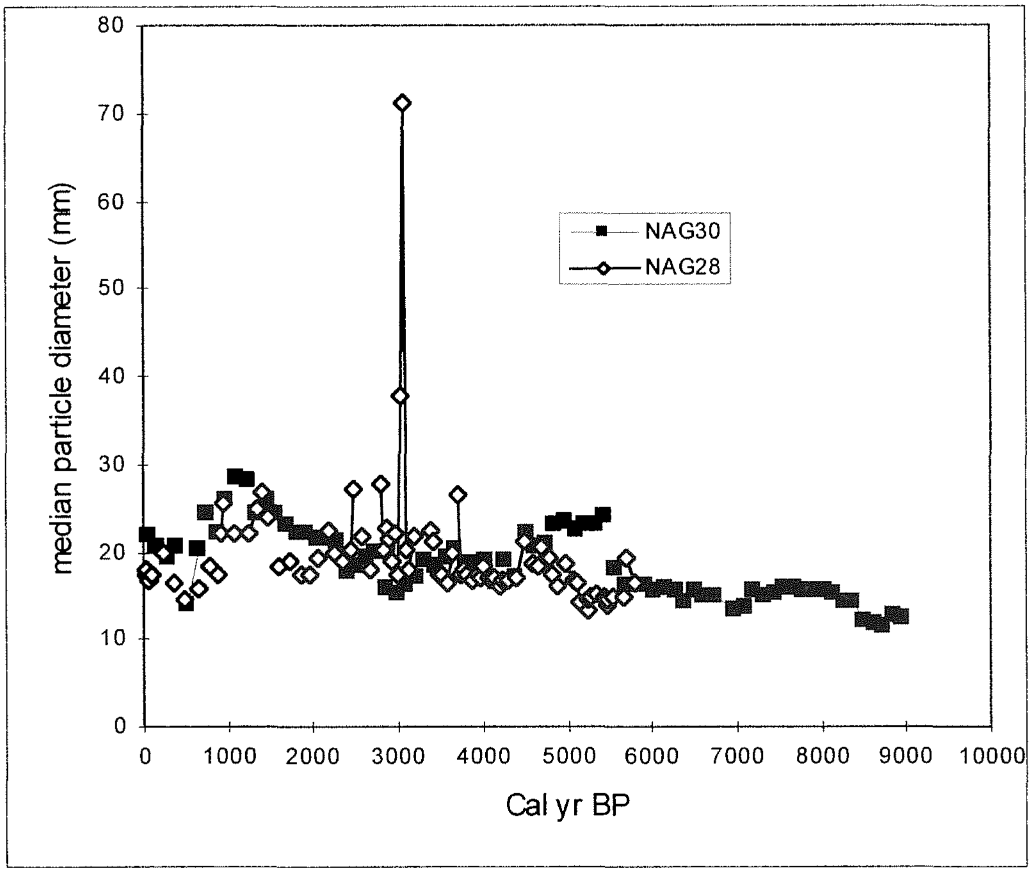


Figure 4.5: Median particle-size properties of Lochnagar sediment cores NAG28 and NAG30.

4.1.2.3 Discussion

Three types of material control the particle-size distribution of Lochnagar sediments. First, coarse (sand) sized particles produce the right hand peaks seen most clearly in the particle size plots of Figure 4.4 c, d and e (note the uni-, bi- and tri-modal distributions). Secondly fine (clay) sized particles give the left-hand tail in Figures 4.4 a-f. Both the sand and clay fractions appear to be catchment derived. Both these materials can be attributed to catchment sources. Thirdly diatoms preserved in the sediment form the sharp silt sized peaks, seen most clearly in the particle size plots of Figure 4.4 b, c and f. Over time there have been large changes in the proportions of diatoms to catchment materials preserved in the Lochnagar sediment.

The cause of the changes in magnetic properties, particularly the increase of magnetic particles in the uppermost sediments (Figure 4.6), remains to be determined. It may have been caused by (i) an increase in atmospheric pollution particles or by (ii) dissolution effects or by (iii) a catchment erosion effect.

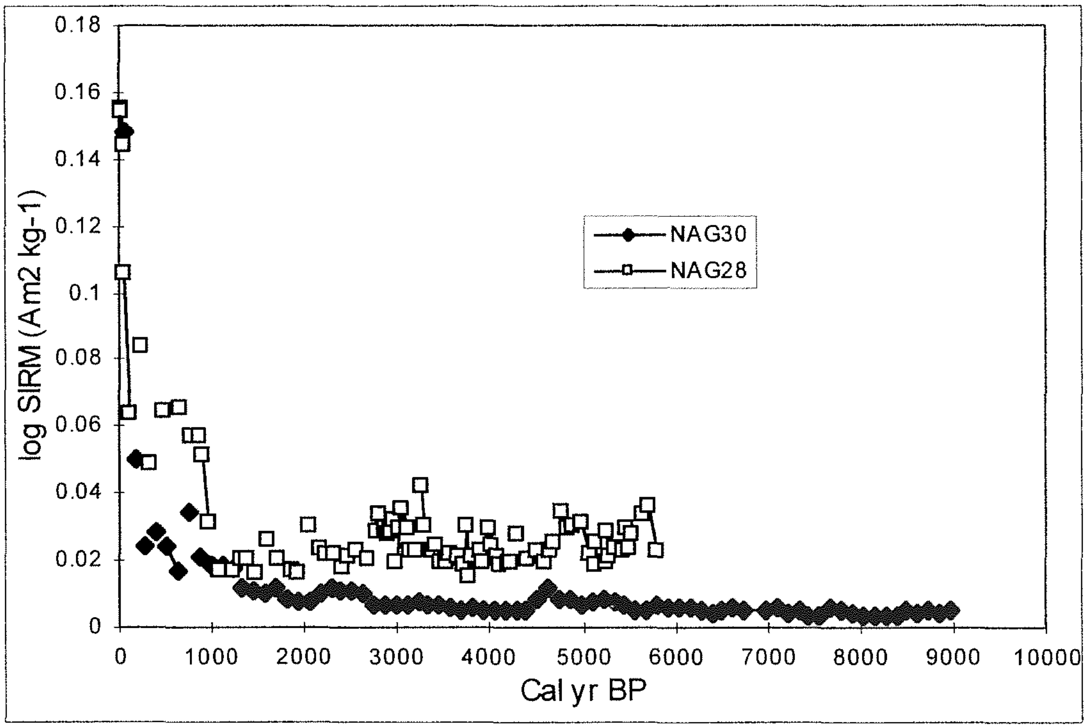


Figure 4.6: Magnetic properties (concentration of SIRM) of Lochnagar sediment cores NAG28 and NAG30.

4.1.3 Sediment Geochemistry - J.A. Scott & R.P. Evershed, School of Chemistry, University of Bristol

4.1.3.1 Bulk Analyses

Biomarker studies (quantitative identification of organic matter) were conducted on the sediment collected from Lochnagar. Lipids' retention of their biological heritage has earned them the name "biomarkers" and the abundance and distribution of these compounds in recent sediments depend on the nature and abundance of their input sources, as well as diagenetic reactions occurring after the death of source organisms (Wünsche *et al*, 1987). Therefore, studies of the organic content of sediment as a function of its depth can provide information about the palaeoenvironmental history of the lake (Meyers and Ishiwatari, 1993). It is hoped that the sediment record of this remote lake will provide a continuous, ecologically and climatically sensitive, high-resolution record of climate variability.

Total organic carbon content of the NAG28 core varies between 1.2 and 17.6% with the lowest amount occurring between 70 and 100 cm depth (Figure 4.7). Nitrogen content tends to follow the trend of organic carbon (Figure 4.8), and indeed, both plots are similar to that for loss on ignition (Figure 4.2).

Carbon/nitrogen ratios show large variation in the uppermost sediment, however values below 20 cm are fairly constant with an average of about 15 (Figure 4.9). The sequence shows small variations in $\delta^{13}C_{TOC}$ with an amplitude of less than $3^0/_{00}$ (-26.3 to $-23.4^0/_{00}$) (Figure 4.10). The heaviest values occur around 80 to 100 cm and coincide with low organic carbon content.

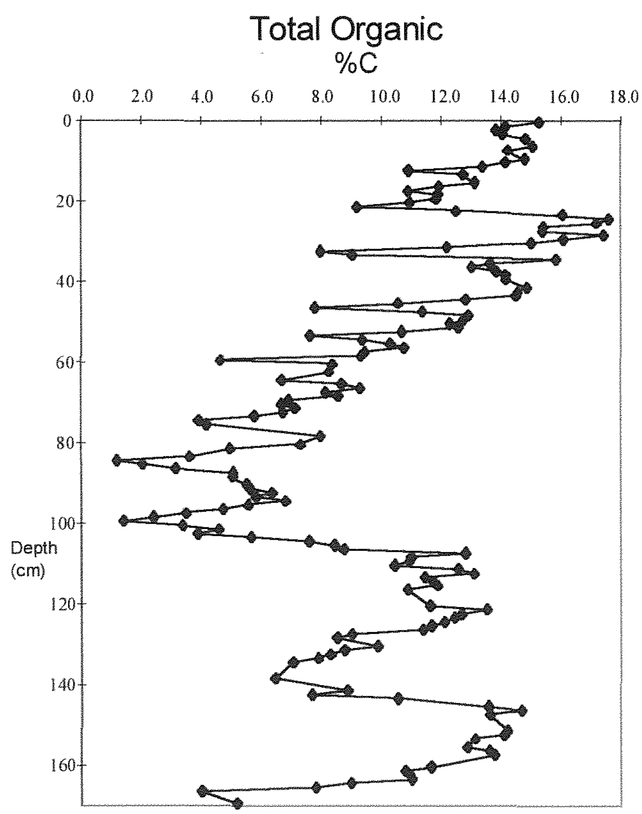


Figure 4.7: Total organic carbon (NAG28)

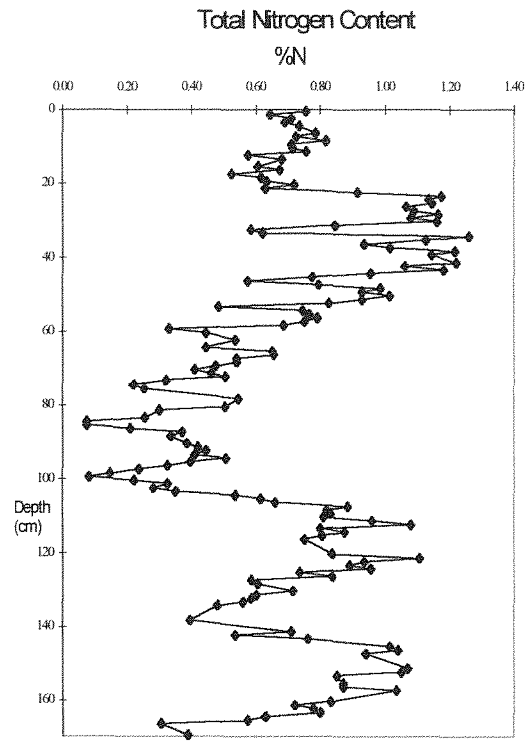


Figure 4.8: Total nitrogen (NAG28)

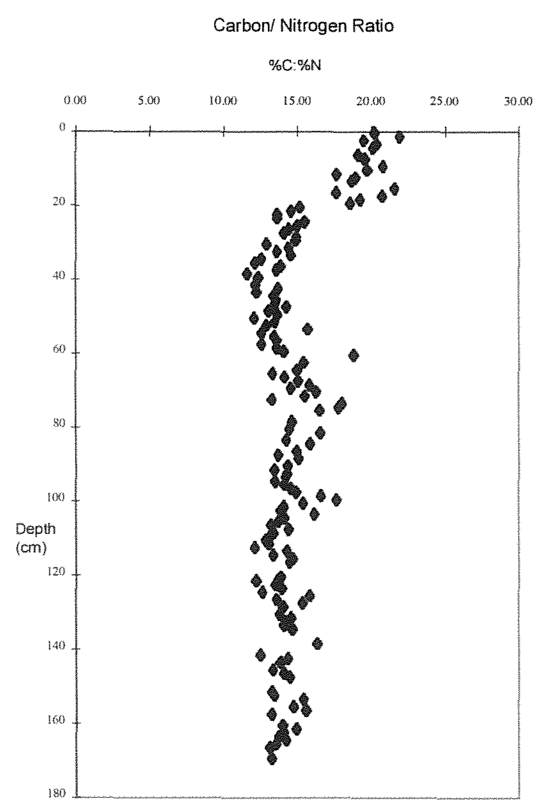


Figure 4.9: Carbon/nitrogen ratios (NAG28)

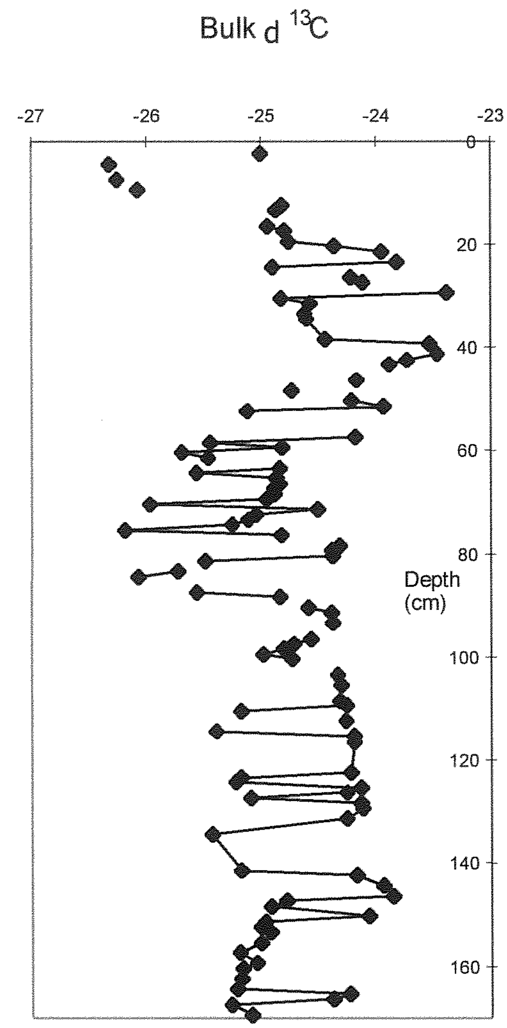


Figure 4.10: Bulk $\delta^{13}C_{TOC}$ (NAG28)

4.1.3.2 Lipid Analyses

The hydrocarbon distribution (C_{19} to C_{33} *n*-alkanes) of NAG28 shows an odd-over-even carbon number predominance and is dominated by long-chain alkanes, suggesting mainly terrigenous input (Cranwell, 1978). A number of bacterial hopanoids have been identified (Figure 4.11) however these occur in low relative abundance and their concentration distributions may not be reliable as a productivity indicator (see Appendix 1).

A plot of total *n*-alkane concentration downcore (Figure 4.12) shows two maxima, however because this signal is dominated by higher plant hydrocarbons and most likely reflects the extent of peat inwash from the catchment, variations observed are not representative of conditions within the lake at a given time. A compound or compound class of autochthonous origin, and occurring in relatively high abundance will provide a more appropriate climate signal for Lochnagar.

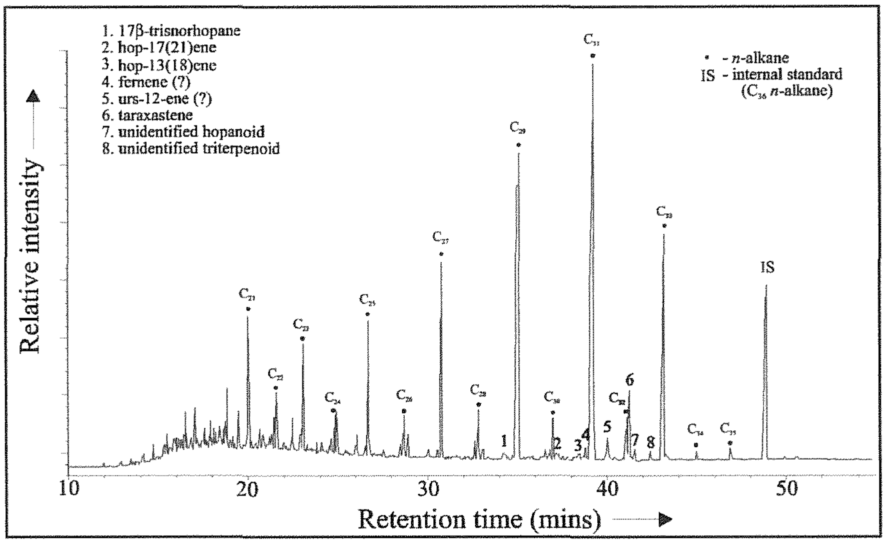


Figure 4.11: Partial gas chromatogram of hydrocarbon fraction from NAG28 at 148 cm depth (5150 cal yr BP)

The acid fractions of NAG28 are also dominated by straight-chain compounds, the *n*-alkanoic acids showing even-over-odd predominance and a bimodal distribution, with maxims at C_{16} and C_{24}. Cranwell (1974) concluded that autochthonous material was the main source of C_{12} - C_{18} alkanoic acids in a lake sediment while terrestrial sources provided their longer-chain counterparts. The relative contribution of these two sources depends on the trophic status of the lake and the rate of erosion of the drainage basin respectively. Figure 4.13 shows a downcore plot of short-chain vs long-chain alkanoic acids in NAG28: while most variation is apparent in the long-chain acid distribution, the distribution of both C_{16} and C_{18} alkanoic acids may prove interesting when compared with other proxies.

Even-carbon-numbered components dominate the distribution of *n*-alkanols in NAG28, the major *n*-alkanol being the C_{24} homologue. Each alcohol fraction, however, is dominated by a C_{30} 4-methyl stanol (Figure 4.14) which could prove a useful indicator for microalgae, and thus lake productivity, as several 4-methyl sterols have been found in diatoms (Volkman *et al*, 1993).

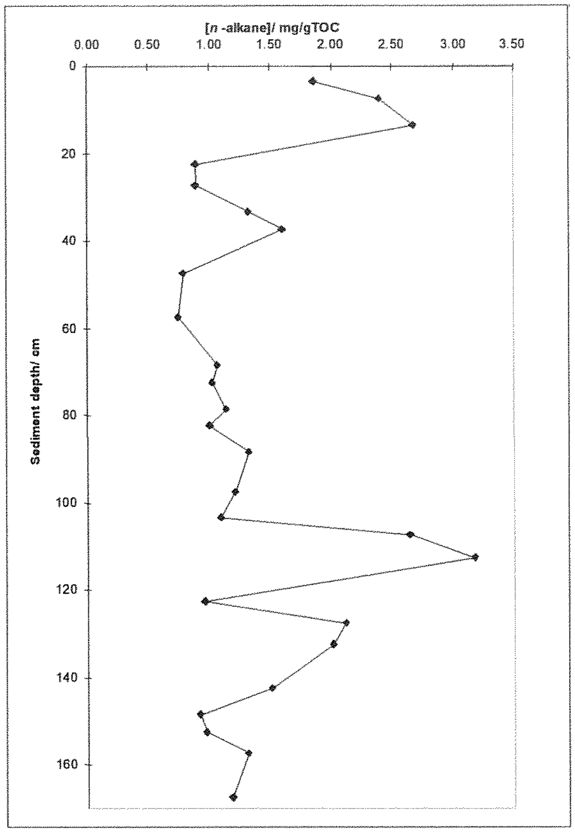


Figure 4.12: Total *n*-alkanes in NAG28

A number of other sterols, such as dinosterol (C_{30}), sitosterol and stigmastanol (both C_{29}) have been identified in the alcohol fraction, however these have not yet been quantified. The C_{29} sterols are of terrestrial origin (Nishimura, 1977) but dinosterol (see Appendix 1) is known as originating from dinoflagellate communities (Robinson *et al*, 1984).

The chlorins distribution in NAG28 (Figure 4.15) shows a maximum at 47 cm sediment depth. These diagenetic products of chlorophyll are of autochthonous origin and should provide information about the productivity of the lake, and thus palaeoclimate.

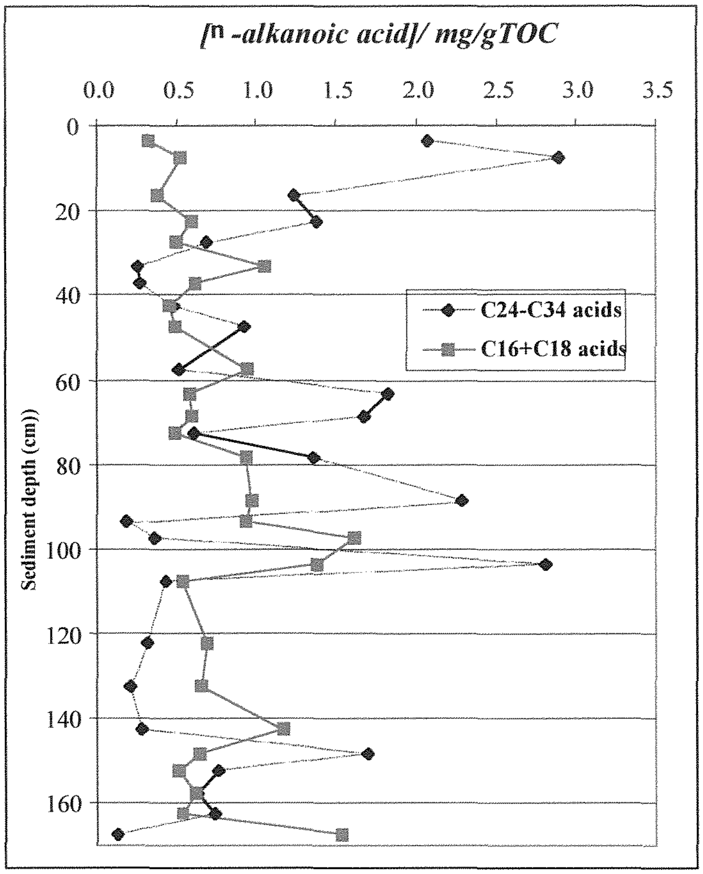


Figure 4.13: NAG28 Long-chain vs short-chain acids

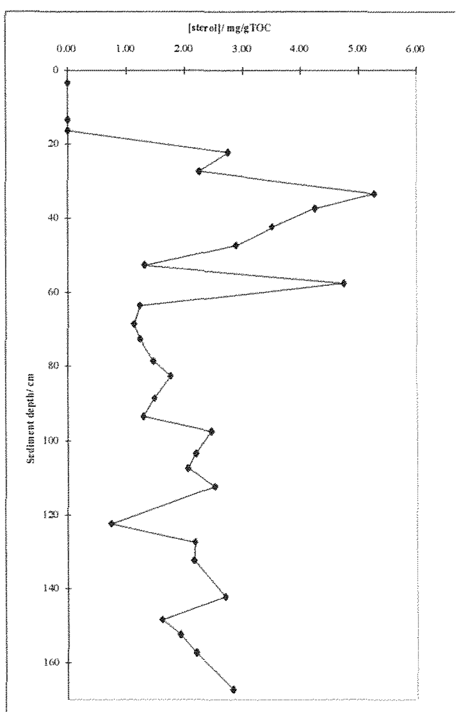


Figure 4.14: 4-methyl stanol distribution in NAG28

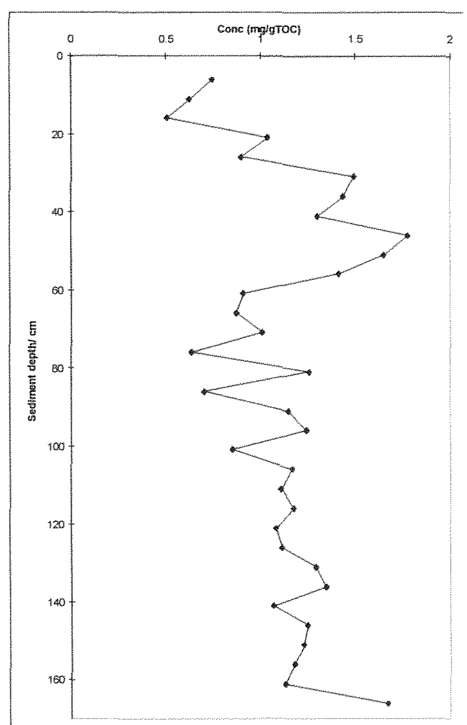


Figure 4.15: Chlorins distribution in NAG28

4.1.3.3 Future Work

1. Further identification of the sterols in the alcohol fraction is required, as well as investigation of other fractions e.g. ketones. Esterified lipids may not have been extracted by the method used: a saponified total lipid extract analysed by high temperature GC may show bound lipids.

2. Although 20 plant and peat samples have been collected from Lochnagar, it has been decided to analyse only the peat and aquatic plants to distinguish between lake-derived lipids and lipids washed into the lake from the catchment.

3. Compound specific carbon isotopic analysis has been carried out on NAG28 alkanes (results not yet edited) and the alcohol fraction is still to be done. Deuterium isotopes have been found to correlate with rainfall (Xie *et al.*, 2000) and various fractions will be analysed using this technique.

4. Chlorin concentrations will be determined at much higher resolution, to provide a detailed productivity record and LC-MS will be used to identify the individual pigments.

4.2 Chronology

Three different methods were available to provide a sediment chronology for the Lochnagar lake sediment cores. These were pollen stratigraphy, tephrachronology and AMS radiocarbon (^{14}C) dating. The results of pollen analysis and AMS radiocarbon dating were complete for the production of the final report.

4.2.1 Pollen - S.M. Peglar & H.J.B. Birks, University of Bergen, Norway

The pollen-stratigraphical data from cores NAG27 and NAG30 are plotted along with the available radiocarbon dates, calibrated dates and the pollen zonation in Figures 4.16 and 4.17. All stratigraphical plots were drawn using the computer program TILIA-GRAPH written by E.C. Grimm.

4.2.1.1 Numerical analyses

Principal components analysis (PCA) of the total pollen-stratigraphical data (Figure 4.18) shows that the stratigraphies of the two cores overlap in terms of overall pollen composition. In this plot of sample scores on PCA axes 1 and 2 with distance biplot scaling, samples of similar pollen composition are positioned close together, given the constraint that the plane formed by the two PCA axes captures 55.2% of the total variance in the data (axis 1 = 38.9%, axis 2 = 16.2%, axis 3 = 5.9%, axis 4 = 3.3%). There is clear overlap between samples from 93.5 (5400 cal yr BP) - 129.5 cm (7550 cal yr BP) in NAG30 and samples from 145.3 (5230 cal yr BP) - 177.3 cm (6250 cal yr BP) in NAG27. Sequence slotting of the two sequences suggests a close match between 167.3 cm (5940 cal yr BP) in NAG27 and 121.5 cm (7050 cal yr BP) in NAG30 with a psi value of sequence discordance of 1.87. These levels are marked in both cores by a decrease in *Ulmus* pollen values from 3-5% to 1%, the first occurrence of *Plantago lanceolata* pollen, and the first rise of Gramineae pollen to values of 4% or more. Although there are strong palynological similarities at these levels in the two cores, the estimated ages seem, at first sight, to be rather different. However, the age-depth models are not without model error and the estimated 95% confidence intervals for the age estimate for 167.3 cm in NAG27 (5425 - 6425 cal yr BP) and for 121.5 cm (6205 - 7870 cal yr BP) overlap. The core correlation suggested by sequence slotting using the observed pollen stratigraphy of NAG27 and NAG30 is thus confirmed by the overlap in the estimated ages and their associated 95% confidence intervals.

Given that the uppermost 10 samples in NAG30 overlap in pollen composition with the lowest 5 or 6 samples in NAG27, these 10 samples in NAG30 were deleted in an initial optimal partitioning. They were then included in a second partitioning when the basal 6 samples of NAG27 were deleted. The resulting partitioning with the uppermost 10 NAG30 samples excluded or included and the lowermost 6 NAG27 samples included or excluded were then evaluated. In both partitionings the zonation for NAG27 and NAG30 combined was the same, but with a partition at 171.3 cm (6055 cal yr BP) in NAG27 in analysis 1 and at 120.5 cm (7035 cal yr BP) in NAG30 in analysis 2. Comparison with the broken-stick model suggests 4 statistically significant zone boundaries in the combined sequence with the same boundary (zone NAG-2/NAG-3) repeated in the two cores. The zonation into local pollen-assemblage zones is shown on Figures 4.16, 4.17, and 4.20.

Principal components analysis of the combined data and comparison of the eigenvalues of the PCA axes with the broken-stick distribution (Legendre & Legendre 1998) indicates that only PCA axes 1 and 2 are statistically significant. These capture 55.2% of the total variance (468.9) in the pollen data. A correlation biplot (Figure 4.19) of all pollen and spore taxa with scores greater than $|0.4|$ on either PCA axis 1 or 2 illustrates the major correlation structure in the pollen data. A group of taxa have high positive correlations between themselves and with PCA axis 1 (e.g. Gramineae, *Plantago lanceolata, Calluna vulgaris, Carex*-type, *Vaccinium*-type, *Rumex acetosella*-type, Rubiaceae), all of which have pollen percentages increasing towards the top of NAG27. There is a group of taxa with high positive correlations between themselves and with PCA axis 2 (e.g. *Betula*, *Populus tremula*, *Salix* undiff., *Dryopteris filix-mas*-type). This group is largely uncorrelated to the previous group on PCA axis 1. *Corylus avellana, Juniperus communis* and *Ulmus* have high positive correlations between themselves and high negative correlations with PCA axis 1, whereas *Alnus glutinosa*, *Fraxinus excelsior* and, to a lesser extent, *Quercus* and *Pinus sylvestris* have a high internal covariance and are negatively correlated with PCA axis 2. This correlation structure summarises the major stratigraphical patterns in the pollen data (Figures 4.16 and 4.17) with taxa that increase together from the beginning of zone NAG-3 towards the present-day (e.g. *Calluna vulgaris*), widespread pollen and spore types with their highest values in zone NAG-1 (e.g. *Betula*), taxa with their maximal values in zone NAG-2 (e.g. *Pinus, Quercus*), and taxa with their highest values in zones NAG-1 and NAG-2 (e.g. *Corylus avellana*). These broad groupings of taxa based on their stratigraphical covariances also differ in their edaphic demands, shade tolerance, and abilities to withstand disturbance.

The individual sample scores are plotted stratigraphically on Figure 4.20, along with the local pollen zonation. The scores are scaled to reflect the relative magnitude of PCA axes 1 and 2. PCA axis 1 (38.9%) parallels the total tree and shrub pollen curve in Figures 4.16 and 4.17 and reflects the progressive decline in tree and shrub cover in the pollen-source area of the loch over the last 9000 years. PCA axis 2 (16.2%), with high positive scores for taxa such as *Betula, Dryopteris filix-mas*-

type, *Salix* undiff., *Populus tremula,* and *Corylus avellana* may reflect the long-term change in soil-type within the loch's catchment, from moderately fertile brown-earth soils in zone NAG-1, a change to less fertile podsols with moder or mor humus in zone NAG-2, and the development of acid podsols and shallow peat in zone NAG-3. Soil erosion, burning, and grazing during zones NAG-4 and NAG-5 may have favoured some plants of more open mineral soils with a slightly higher base-demand. The two major underlying gradients of variation in the pollen-stratigraphical data are thus a gradient of decreasing tree and shrub cover and associated change in light and shade conditions and a gradient of changing soil fertility from brown earths to podsols and shallow peat to more open soils in the last 1400 years.

4.2.1.2 Vegetational history

4.2.1.2.1 Botancial background

Lochnagar lies within an impressive corrie at 783 m altitude with steep, often vertical back-walls (up to 240 m high) consisting of acid granite. The corrie faces north-east and today supports a mosaic of sparse vegetation (*ca.* 60% cover) dominated by dwarf, prostrate *Calluna vulgaris* and stunted *Vaccinium myrtillus*, with some *V.vitis-idaea, V.uliginosum, Empetrum nigrum* spp. *hermaphroditum,* and *Arctostaphylos uva-ursi* on well-drained skeletal, ranker, or thin podsolic soils, alternating with areas dominated by *Scirpus cespitosus, Eriophorum vaginatum, Molinia caerulea,* and *Nardus stricta* on shallow peat. In wind-exposed areas *Loiseleuria procumbens, Juncus trifidus*, and *Carex bigelowii* are locally common. Extensive areas of stable block-scree below the cliffs support ferns such as *Athyrium distentifolium, Cryptogramma crispa, Blechnum spicant, Dryopteris assimilis,* and *D.abbreviata*, often growing with *Luzula sylvatica* and shaggy *Calluna vulgaris*. On some of the broader ledges on the cliffs, ungrazed vegetation dominated by tall herbs such as *Filipendula ulmaria, Rumex acetosa, Silene dioica, Luzula sylvatica, Trollius europaeus, Cirsium heterophyllum, Oxalis acetosella, Cochlearia officinalis, Geranium sylvaticum, Sedum rosea, Angelica sylvestris, Geum rivale, Oxyria digyna,* and *Saussurea alpina* occurs locally. *Cicerbita alpina, Saxifraga rivularis*, and *Gnaphalium norvegicum* are national rarities that occur on ledges and gullies near the Black Spout. The flora and vegetation of the corrie surrounding the loch are strongly montane in character, with affinities to the sub-alpine and low-alpine zones of western Norway today. Lochnagar lies above the known natural tree-limit in this part of Scotland today (*ca.* 650 m), although seedlings of pine and birch can very rarely be found as high as 850 m on crags and sheltered rock outcrops and fossil stumps occur as high as 790 m in the area.

In their reconstruction of the potential vegetation of the Scottish Highlands, McVean and Ratcliffe (1962) proposed that Lochnagar itself was at or near the tree-line and that the valleys to the south and east were dominated by *Betula* to about 650 m, by *Pinus sylvestris* to about 550 m, and by *Quercus* spp. to about 400 m.

The status of *Quercus* spp. in this part of Scotland is obscure. There are several small oak woods on Deeside, for example at Craigendarroch at Ballater at *ca.* 250 - 350 m, at Crathie at *ca.* 350 m, and at Dinnet at *ca.* 200 m. These woods have tall, well-grown trees over 100 years old and although they have been coppiced, they have the appearance of being semi-natural, with a 'typical' associated flora of shrubs, dwarf-shrubs, herbs, grasses, bryophytes, and lichens.

4.2.1.2.2 Inferred vegetational history

Even though there are no trees in the catchment of the loch today, the modern pollen deposition contains about 40% tree and shrub pollen (mainly *Betula* but with surprisingly low *Pinus* values and high values of *Corylus avellana* and *Alnus glutinosa*). It is many kilometres to the nearest *Corylus* bushes. *Alnus glutinosa* occurs locally in the valleys near Lochnagar at about 300 m, for example in Deeside, Glen Esk, and Glen Clova. The modern pollen assemblage suggests that the relevant pollen-source area of the loch is very large, and much greater than the theoretic expectation based on Sugita's (1994) pollen-representation model that would predict a source area with a radius of about 500 - 800 m from the loch's margin. It seems that today (and one presumes in the past too) the relevant pollen-source area is likely to have a radius of several km. If this is correct, then interpretations of the pollen stratigraphy at Lochnagar in terms of the vegetational history of the corrie are very difficult and are largely conjectural, and are likely to be erroneous.

The lowest pollen zone (NAG-1) with a basal date of 8430 ± 80 radiocarbon years BP and a modelled age of *ca.* 9030 cal yr BP may reflect the local occurrence of fern-rich *Betula* and *Corylus* scrub with some *Populus tremula, Sorbus aucuparia*, and *Salix* growing on fertile brown-earth soils in or near the corrie. Tall-herbs such as *Angelica, Filipendula, Urtica*, and *Rumex acetosa* may have grown in such stands, as they do today in high-altitude birch woods in Glen Clova and on Deeside.

Pinus sylvestris and, a little later, *Alnus glutinosa* pollen values rise in NAG-2 (*ca.* 8350 cal yr BP). These rises reflect the arrival and expansion of these trees in this part of Scotland from about 8400 calibrated years BP (Birks, 1996; Bennett, 1996b). Pine certainly grew near the loch during the Holocene as pine stumps occur in eroding peat near the outflow and along the Lochnagar Burn at about 700 m. Rapson (1985) obtained a radiocarbon date of 6080 ± 50 radiocarbon years BP (= 6900 cal yr BP) for a pine stump near the eastern shore of the loch. It is possible that during zone NAG-2 the corrie was lightly wooded with sub-alpine birch scrub associated with *Salix* spp., *Populus tremula, Sorbus aucuparia,* and *Juniperus communis*, abundant ferns, and some tall-herbs on the slopes and block-screes below the cliffs. Small stands of stunted pine may have occurred locally, including the peaty areas near the loch. It is unclear if *Alnus glutinosa, Quercus* spp., *Ulmus*, or *Fraxinus excelsior* grew near the loch at this time. Overall on ecological grounds it seems unlikely. These trees may have extended their altitudinal ranges by about 200 m if early- and mid-Holocene mean summer temperatures were about 1.5 - 2°C higher than today. Given such an elevational rise, their upper altitudinal limits may have been 500 - 600 m, about 200 m lower than the loch.

The zone NAG-2/NAG-3 transition (*ca.* 6000 - 6500 cal yr BP) is marked by the decline in *Ulmus* pollen percentages. This decline presumably reflects the widespread decrease of *Ulmus* pollen regionally that occurred throughout much of the British Isles and parts of north-west Europe in the mid-Holocene.

Zones NAG-3, NAG-4, and NAG-5 show progressively increasing values of Gramineae, *Carex*-type, *Calluna vulgaris,* and *Vaccinium*-type pollen and correspondingly decreasing percentages of tree pollen, especially *Pinus, Quercus,* and *Corylus avellana*. These changes are interpreted as reflecting the progressive loss of woodland and scrub in the pollen-source area of the loch and the local and regional expansion of grassland, moorland, heath, and blanket bog, with plants such as *Arctostaphylos, Empetrum nigrum, Rubus chamaemorus, Vaccinium, Melampyrum, Narthecium ossifragum, Ranunculus acris, Rumex acetosa, R. acetosella, Urtica, Huperzia selago,* and *Sphagnum*. The increase in microscopic charcoal particles in the top 25 cm (*ca.* 900 cal yr BP) may reflect 'muir-burning' and the subsequent management of grouse moor, as the charcoal values are closely paralleled by changes in *Calluna vulgaris* pollen values.

The scattered occurrences of pollen or spores of 'alpine' and montane taxa, all of which persist today in the corrie or on the cliff ledges or in the gullies of the surrounding cliffs, indicate their persistence locally during the Holocene. These include *Huperzia selago, Lycopodium annotinum, Diphasiastrum alpinum, Cryptogramma crispa, Selaginella selaginoides, Trollius europaeus, Saxifraga oppositifolia*-type, *S.stellaris*-type, *S. cernua/S.rivularis*, *Sedum* (? *S.rosea*), *Rubus chamaemorus, Cerastium cerastioides*-type, and *Salix herbacea*-type.

The aquatic macrophyte flora of the loch today is sparse, consisting of *Isoetes lacustris* and *Juncus bulbosus* forma *fluitans*. The pollen straigraphy suggests that the macrophyte flora has been similarly impoverished throughout the Holocene, but with the former presence of *Potamogeton* (*Eupotamogeton*) (? *P.natans*), *Ranunculus trichophyllus*-type (? *R.flammula*), and *Sparganium emersum*-type (? *S.angustifolium*). *Isoetes lacustris* may have been commoner in the loch during NAG-1 and part of NAG-2, possibly because of greater water clarity, higher base-status, or warmer temperatures. Lochnagar today is one of the highest known localities for *I.lacustris* in Scotland.

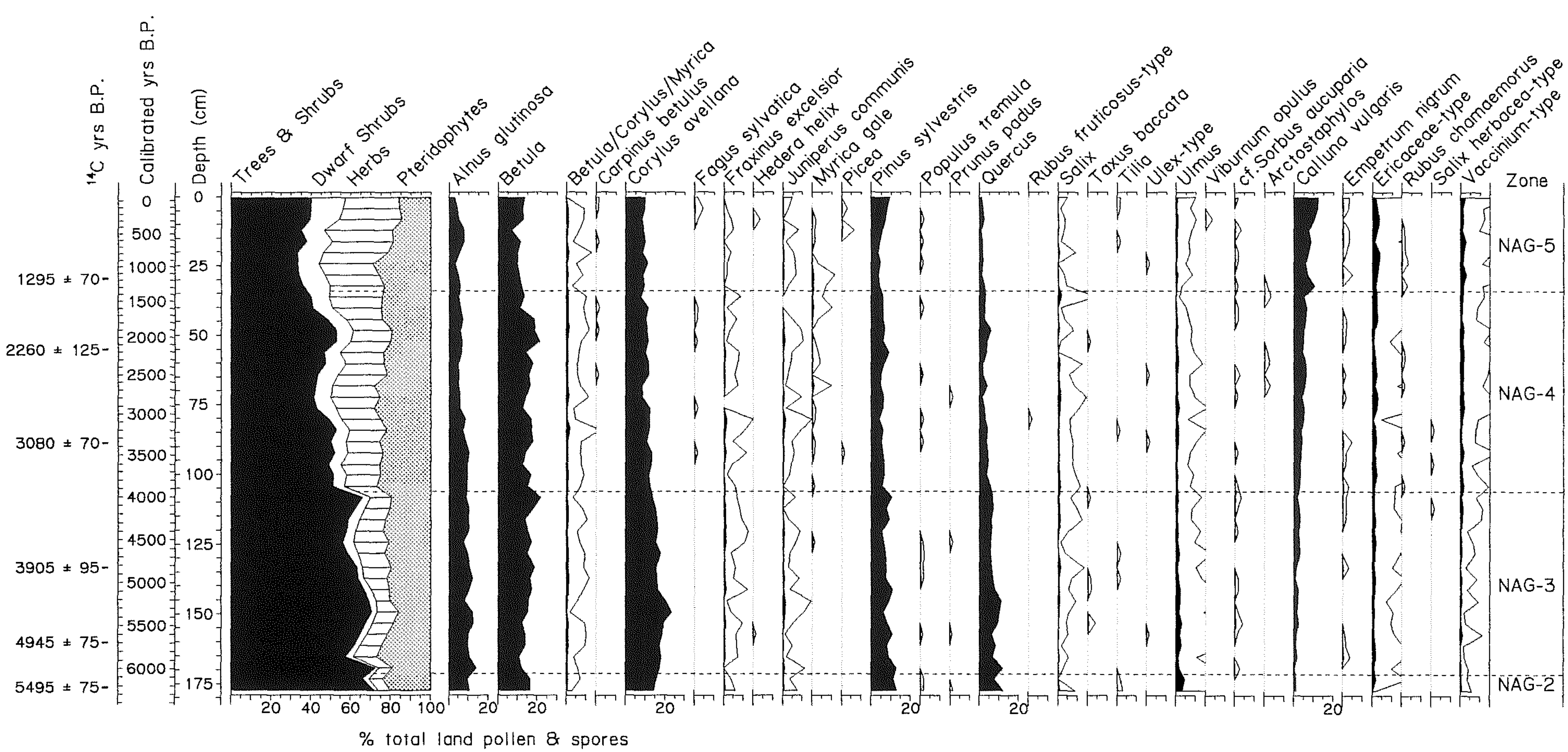
4.2.1.3 Conclusions

The pollen stratigraphy of Lochnagar covers the last 9000 years. It has many unexpected features, nearly all of which are interpretable on the assumption that the relevant pollen-source area of the loch is about two orders of magnitude larger than the theoretical predictions of Sugita's (1994) model. Such a difference is theoretically possible if the local and extra-local pollen deposition is very low at Lochnagar. As a result regional and extra-regional pollen deposition dominates the pollen record at Lochnagar.

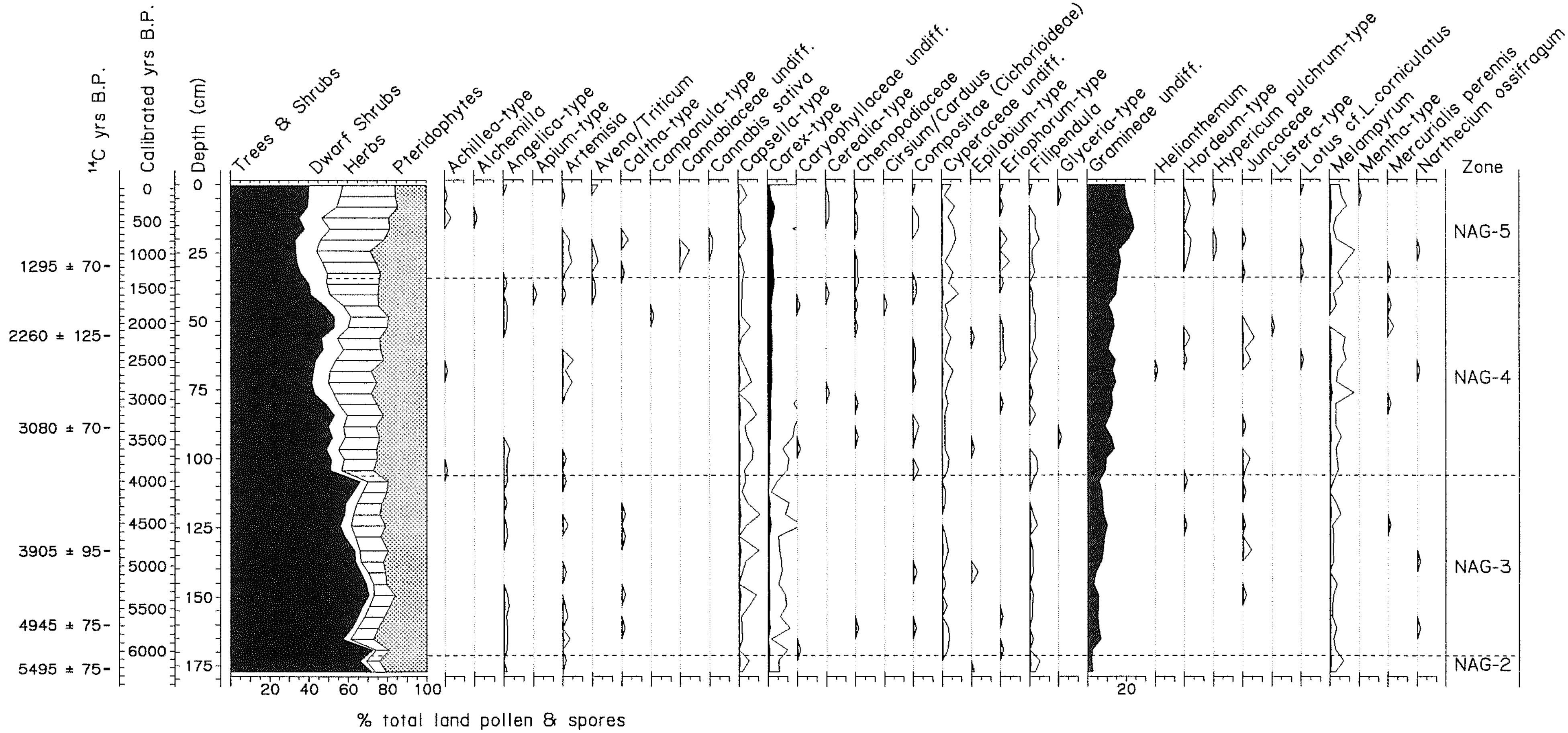
The major patterns of long-term change have been progressive loss of woodland cover and soil deterioration from brown-earths to podsols and shallow peat. The pollen stratigraphy, as interpreted here as reflecting primarily regional and extra-regional pollen deposition, provides no unambiguous evidence for climatic change in the Holocene.

Figure 4.16: Pollen diagram for Lochnagar based on core NAG27. Pollen and spores included in the calculation sum are expressed as percentages of the calculation sum. Other microfossils are expressed as percentages of the calculation sum plus the relevant category. The unshaded curves are x10 exaggeration. The available radiocarbon dates and the modelled sample ages in calibrated year BP are also shown.

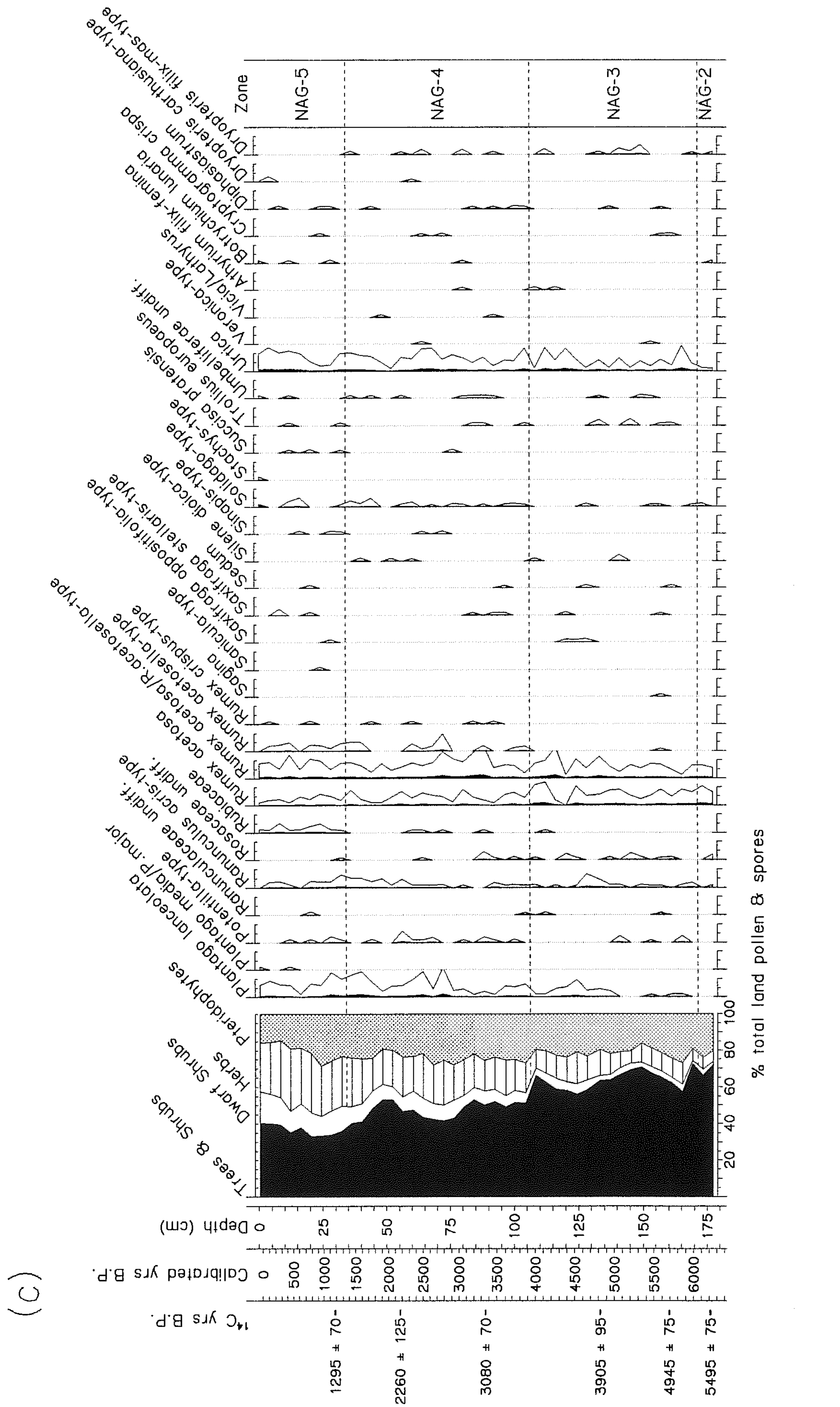
LOCHNAGAR 27
Pollen & spore percentages
Analysed by Sylvia M. Peglar, 1999-2000



(b)



14C yrs B.P.
Calibrated yrs B.P.
Depth (cm)
Trees & Shrubs
Dwarf Shrubs
Herbs
Pteridophytes
Achillea-type
Alchemilla
Angelica-type
Apium-type
Artemisia
Avena/Triticum
Caltha-type
Campanula-type
Cannabiaceae undiff.
Cannabis sativa
Capsella-type
Carex-type
Caryophyllaceae undiff.
Cerealia-type
Chenopodiaceae
Cirsium/Carduus
Compositae (Cichorioideae)
Cyperaceae undiff.
Epilobium-type
Eriophorum-type
Filipendula
Glyceria-type
Gramineae undiff.
Helianthemum
Hordeum-type
Hypericum pulchrum-type
Juncaceae
Listera-type
Lotus cf.L.corniculatus
Melampyrum
Mentha-type
Mercurialis perennis
Narthecium ossifragum
Zone
NAG-5
NAG-4
NAG-3
NAG-2
1295 ± 70
2260 ± 125
3080 ± 70
3905 ± 95
4945 ± 75
5495 ± 75
% total land pollen & spores


(C)
¹⁴C yrs B.P.
Calibrated yrs B.P.
Depth (cm)
1295 ± 70
2260 ± 125
3080 ± 70
3905 ± 95
4945 ± 75
5495 ± 75
Trees & Shrubs
Dwarf Shrubs
Herbs
Pteridophytes
Plantago lanceolata
Plantago media/P. major
Potentilla-type
Ranunculaceae undiff.
Ranunculus acris-type
Rosaceae undiff.
Rubiaceae
Rumex acetosa
Rumex acetosa/R. acetosella-type
Rumex crispus-type
Sagina
Sanicula-type
Saxifraga oppositifolia-type
Saxifraga stellaris-type
Sedum
Silene dioica-type
Sinapis-type
Solidago-type
Stachys-type
Succisa pratensis
Trollius europaeus
Umbelliferae undiff.
Urtica
Veronica-type
Vicia/Lathyrus
Athyrium filix-femina
Botrychium lunaria
Cryptogramma crispa
Diphasiastrum
Dryopteris carthusiana-type
Dryopteris filix-mas-type
Zone
NAG-5
NAG-4
NAG-3
NAG-2
% total land pollen & spores

(d)

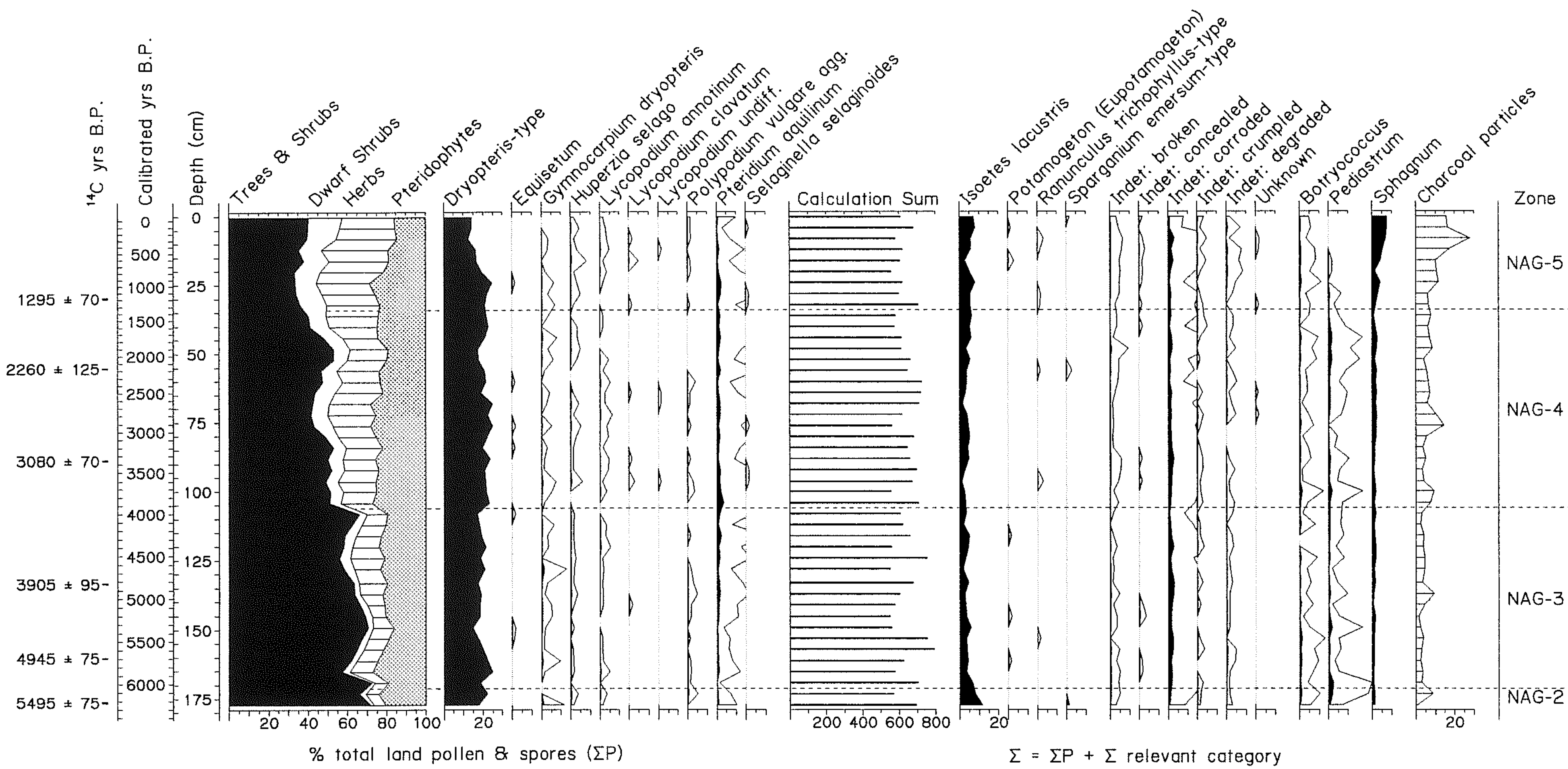
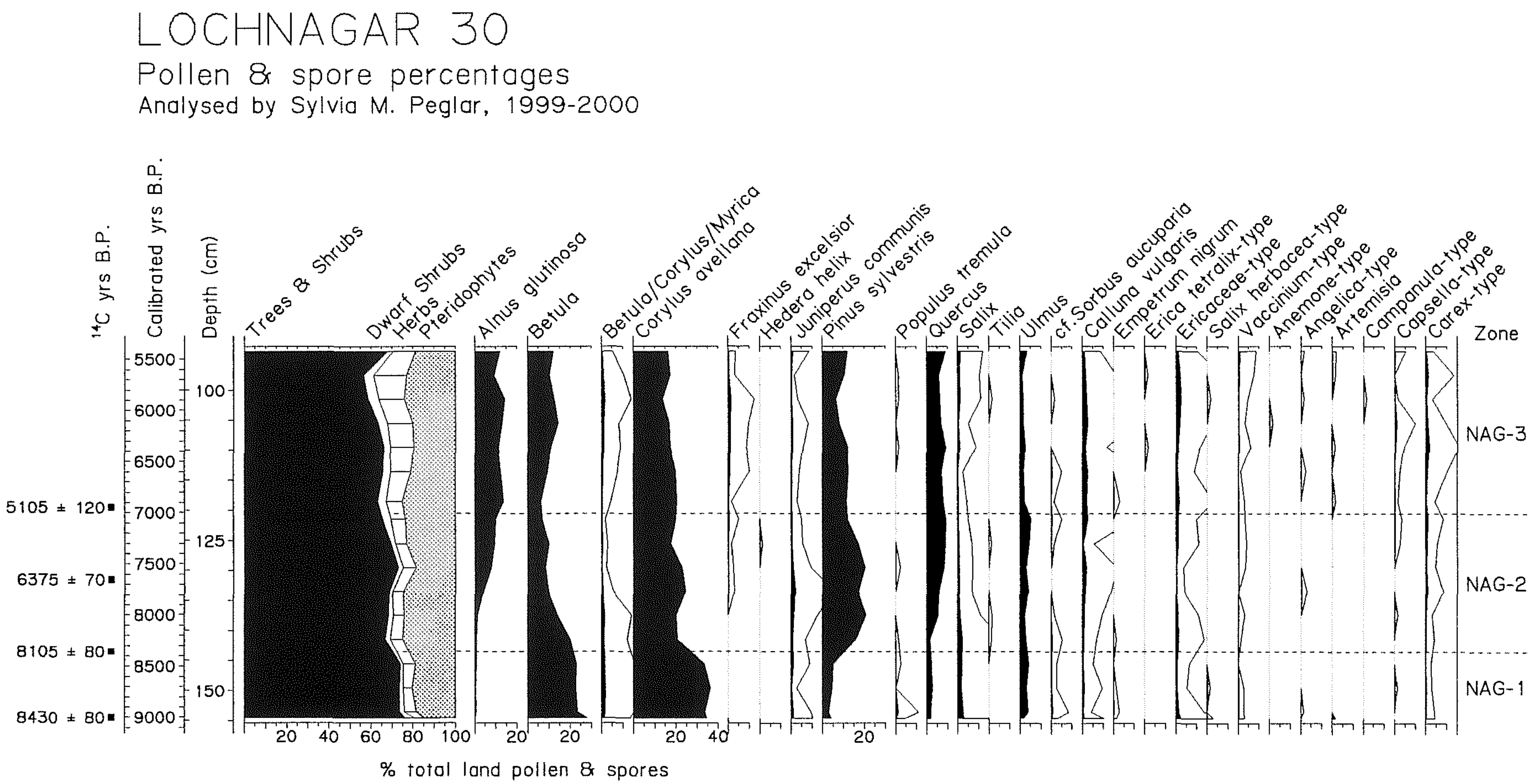
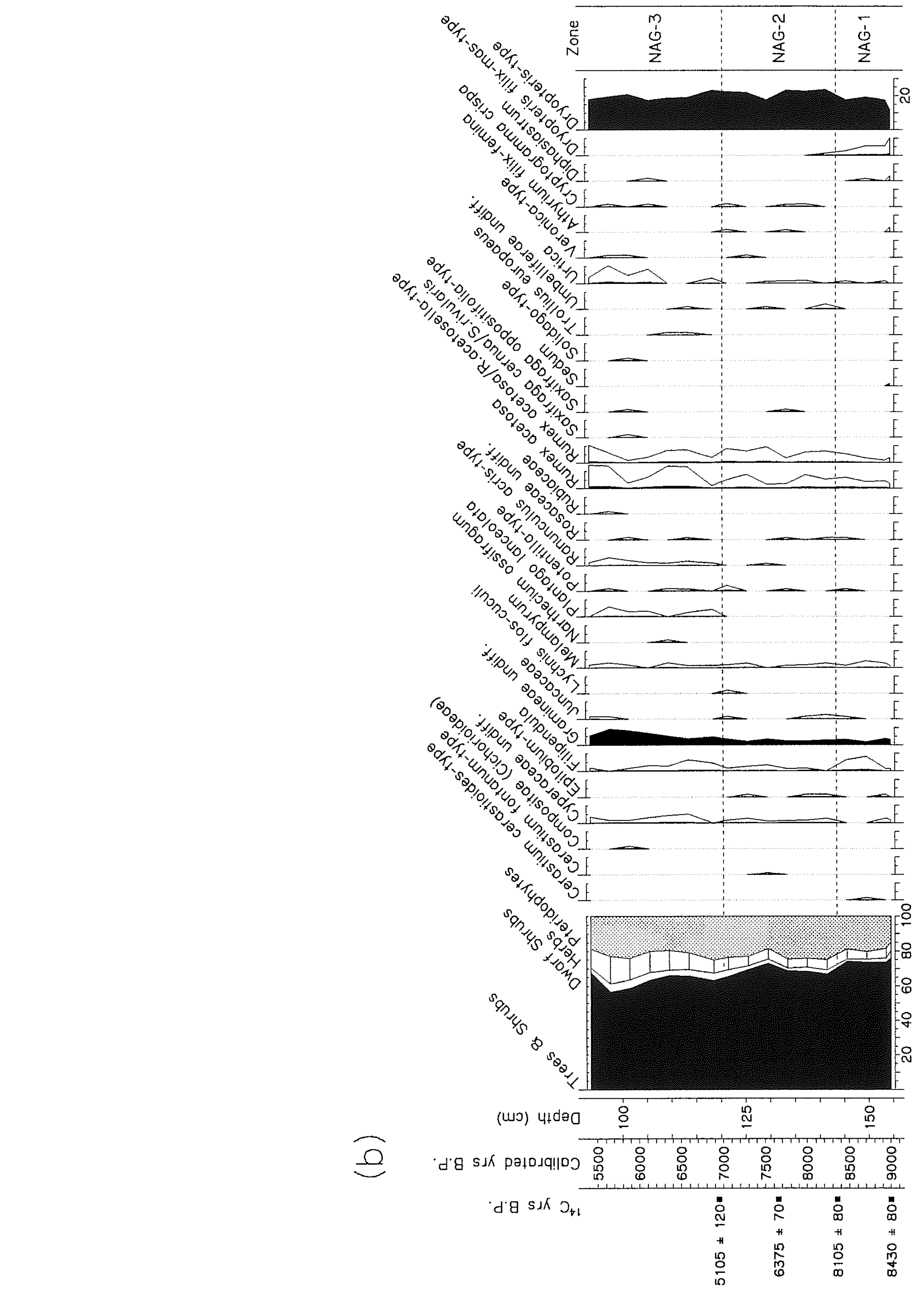

14C yrs B.P.
Calibrated yrs B.P.
Depth (cm)
Trees & Shrubs
Dwarf Shrubs
Herbs
Pteridophytes
Dryopteris-type
Equisetum
Gymnocarpium dryopteris
Huperzia selago
Lycopodium annotinum
Lycopodium clavatum
Lycopodium undiff.
Polypodium vulgare agg.
Pteridium aquilinum
Selaginella selaginoides
Calculation Sum
Isoetes lacustris
Potamogeton (Eupotamogeton)
Ranunculus trichophyllus-type
Sparganium emersum-type
Indet: broken
Indet: concealed
Indet: corroded
Indet: crumpled
Indet: degraded
Unknown
Botryococcus
Pediastrum
Sphagnum
Charcoal particles
Zone
1295 ± 70
2260 ± 125
3080 ± 70
3905 ± 95
4945 ± 75
5495 ± 75
NAG-5
NAG-4
NAG-3
NAG-2
% total land pollen & spores (ΣP)
Σ = ΣP + Σ relevant category

Figure 4.17: Pollen diagram for Lochnagar based on core NAG30. Pollen and spores included in the calculation sum are expressed as percentages of the calculation sum. Other microfossils are expressed as percentages of the calculation sum plus the relevant category. The unshaded curves are x10 exaggeration. The available radiocarbon dates and the modelled sample ages in calibrated year BP are also shown.

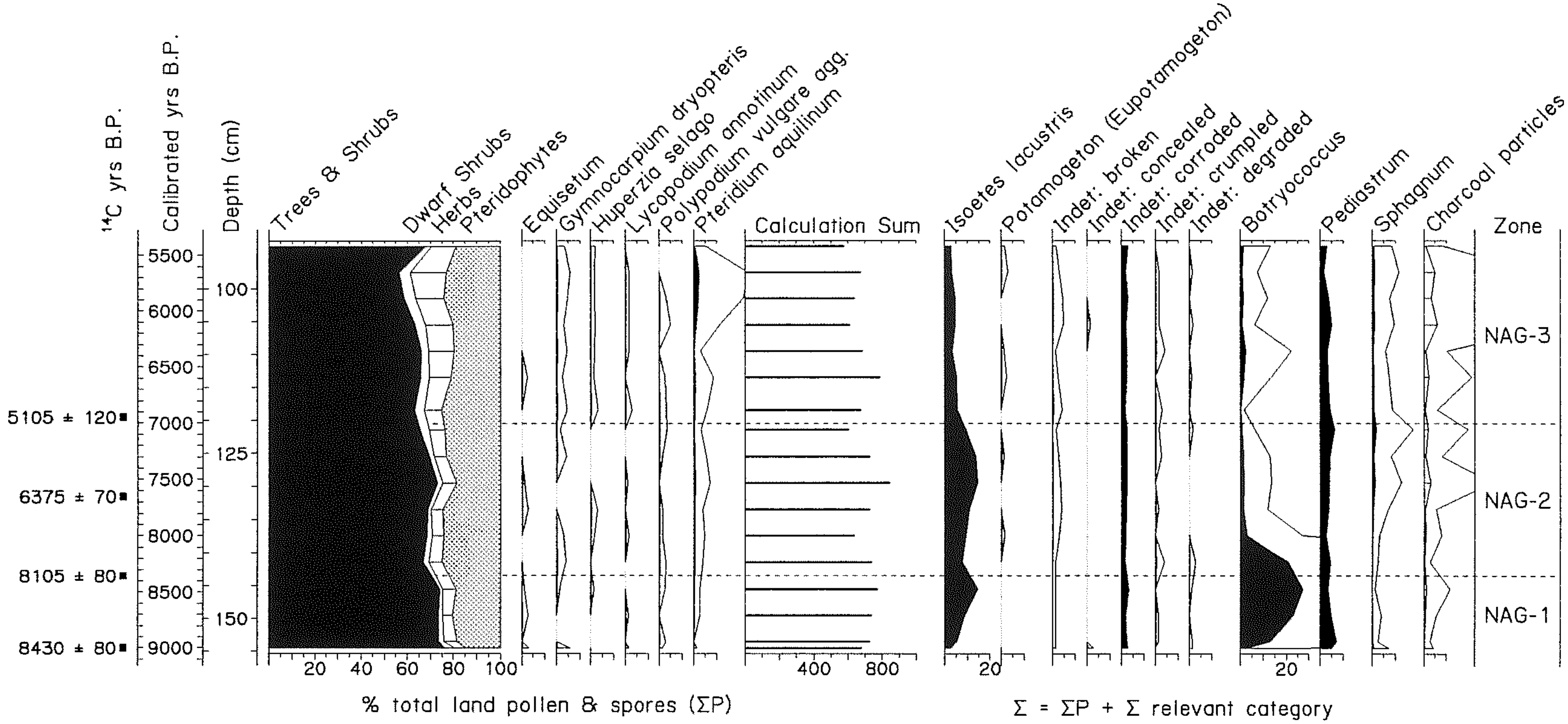


Fig



(b)
14C yrs B.P.
Calibrated yrs B.P.
Depth (cm)
5105 ± 120
6375 ± 70
8105 ± 80
8430 ± 80
5500
6000
6500
7000
7500
8000
8500
9000
100
125
150
Trees & Shrubs
Dwarf Shrubs
Herbs
Pteridophytes
Cerastium cerastoides-type
Cerastium fontanum-type
Compositae (Cichorioideae)
Cyperaceae undiff.
Epilobium-type
Filipendula
Gramineae
Juncaceae undiff.
Lychnis flos-cuculi
Melampyrum
Narthecium ossifragum
Plantago lanceolata
Potentilla-type
Ranunculus acris-type
Rosaceae undiff.
Rubiaceae
Rumex acetosa
Rumex acetosa/R.acetosella-type
Saxifraga cernua/S.rivularis
Saxifraga oppositifolia-type
Sedum
Solidago-type
Trollius europaeus
Umbelliferae undiff.
Urtica
Veronica-type
Athyrium filix-femina
Cryptogramma crispa
Diphasiastrum
Dryopteris filix-mas-type
Dryopteris-type
Zone
NAG-3
NAG-2
NAG-1
20
40
60
80
100
% total land pollen & spores

(C)



^{14}C yrs B.P.
Calibrated yrs B.P.
Depth (cm)
Trees & Shrubs
Dwarf Shrubs
Herbs
Pteridophytes
Equisetum
Gymnocarpium dryopteris
Huperzia selago
Lycopodium annotinum
Polypodium vulgare agg.
Pteridium aquilinum
Calculation Sum
Isoetes lacustris
Potamogeton (Eupotamogeton)
Indet: broken
Indet: concealed
Indet: corroded
Indet: crumpled
Indet: degraded
Botryococcus
Pediastrum
Sphagnum
Charcoal particles
Zone
5105 ± 120
6375 ± 70
8105 ± 80
8430 ± 80
5500
6000
6500
7000
7500
8000
8500
9000
100
125
150
20
40
60
80
100
400
800
20
20
NAG-3
NAG-2
NAG-1
% total land pollen & spores (ΣP)
Σ = ΣP + Σ relevant category

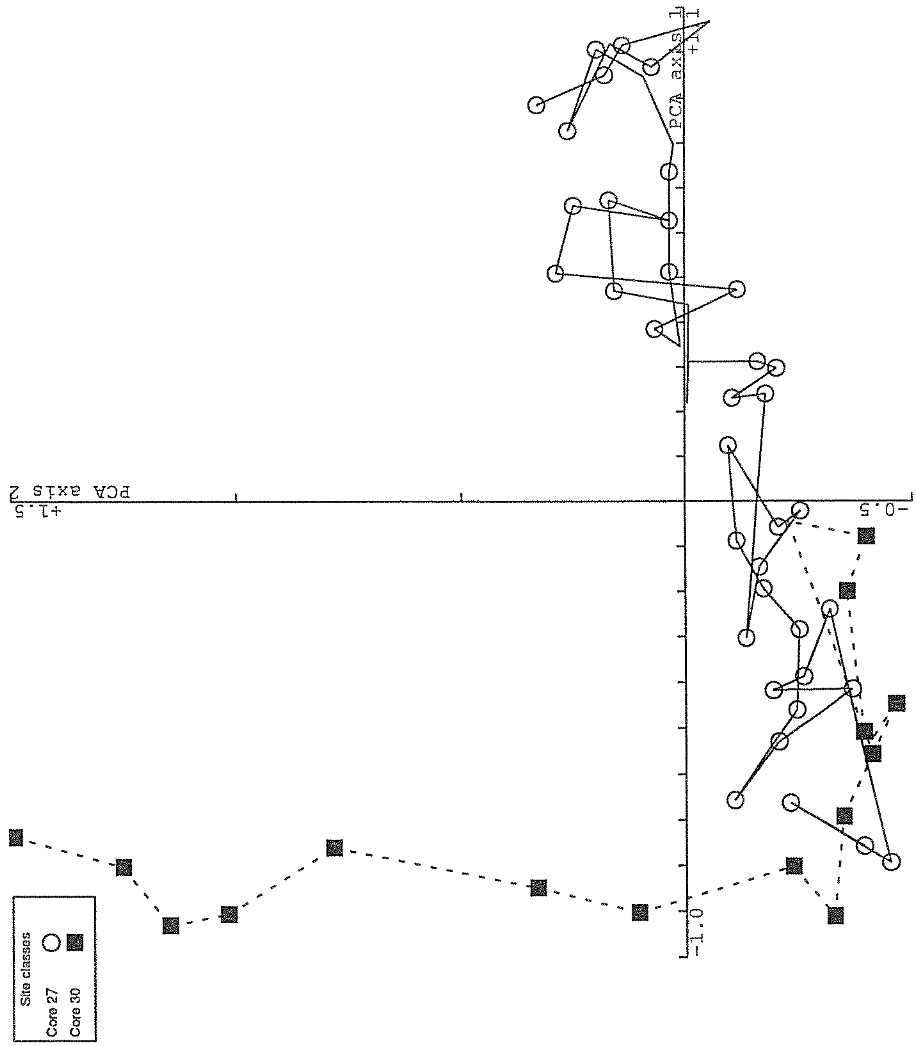


Figure 4.18: Plot of samples from NAG27 and NAG30 on principal component analysis axes 1 and 2. The samples are joined in stratigraphical sequence. Scaling is distance biplot scaling.

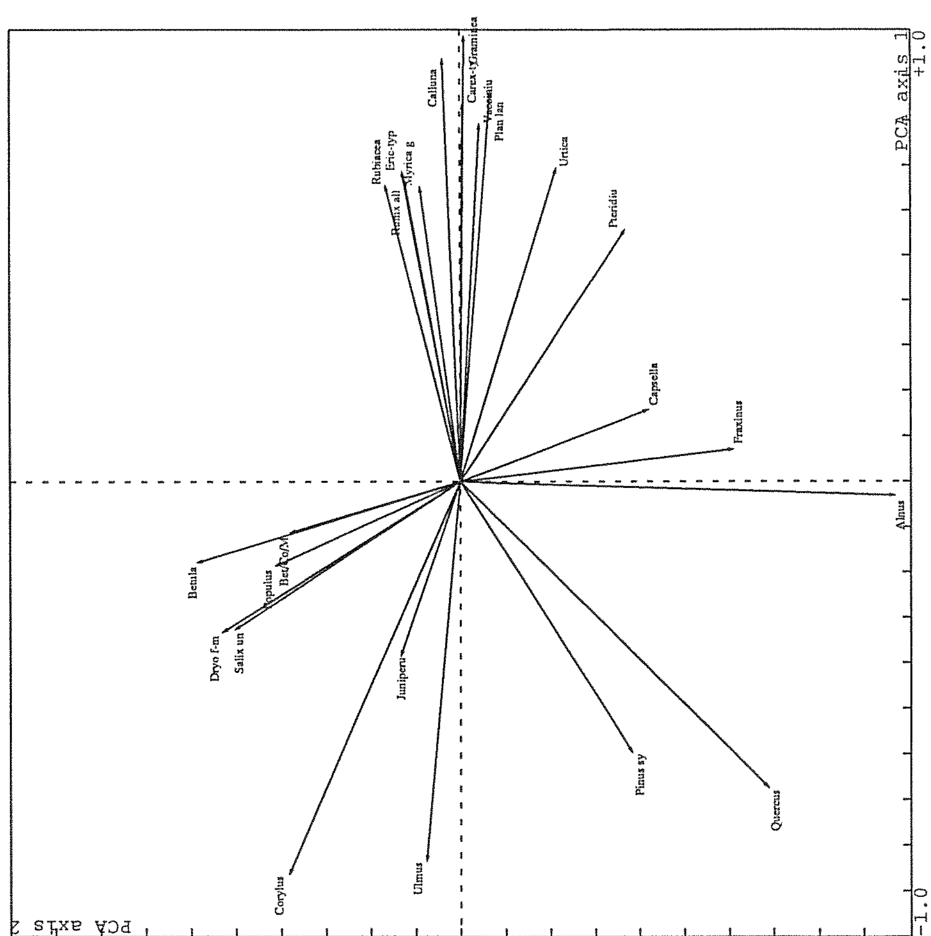


Figure 4.19: Plot of major pollen and spore taxa on principal component analysis axes 1 and 2. Scaling is correlation biplot scaling.

Figure 4.20: Plot of sample scores on principal component analysis axes 1 and 2 plotted stratigraphically. Sample scores are scaled for distance biplots and have been multiplied by x100. The scores for axis 1 have also been reflected.

4.2.2 ^{14}C AMS Dates

Six ^{14}C AMS dates were initially allocated under the CHILL project and an additional four dates were obtained to confirm the pollen inferred chronology. Table 4.1 lists the samples selected for dating from the master core NAG27 and the littoral core NAG30. Because of the limited number of dates available under the CHILL project emphasis was concentrated on the longer chronology in the master core with six AMS dates. The remaining four dates were obtained for samples from the lower part of the littoral core in the expectation that these sediments were older than those in the master core. No dates were obtained for the more recent sediments in the littoral core. The core chronologies were initially estimated using pollen analysis.

The samples were chosen as follows: First, three samples (median, 1st quartile, 2nd quartile) were selected from NAG27. The median sample corresponded to pollen zone NAG-4 and Chironomid zone Nch-2 (see sections 4.2.1 and 4.4). The second quartile sample corresponded to zone Nch-1 and NAG-3. The first quartile sample was altered from 44 cm to 30 cm to correspond to zone NAG-5 and Nch-3 (see below). Two more samples were selected from NAG27 at 55 cm and 160 cm based on changes in the diatom assemblages. Basal sample were selected from both NAG27 and NAG30 to confirm the full age of the sequences as well as dates to confirm the expansion of *Pinus*, the expansion of *Alnus* and the decline of *Ulmus* in NAG30.

Table 4.1: Lochnagar bulk sediment samples sent for ^{14}C AMS dates

NAG27 Sample No.	Core	Sample Interval (cm)	Notes
1.	NAG27	29.6 - 30.0	
2.	NAG27	55.0 - 55.4	
3.	NAG27	88.6 - 89.0	*Median sample*
4.	NAG27	133.2 - 133.6	*2nd Quartile sample*
5.	NAG27	160.0 - 160.4	
6.	NAG27	176.0 - 176.6	*Basal sample*
NAG30			
1.	NAG30	119.0 - 120.0	
2.	NAG30	131.0 - 132.0	
3.	NAG30	143.0 - 144.0	
4.	NAG30	154.0 - 155.0	*Basal sample*

The six ^{14}C AMS dates reveal a *ca.* 5500 year chronology for Lochnagar in NAG27 (Table 4.2). The chronology has a small average age error of approximately 85 years. These results confirmed the estimated dates based on pollen analysis. The expansion of *Pinus* starts at *ca.*

8100 yrs BP, expansion of *Alnus* ca. 6400 yrs BP while the *Ulmus* decline is AMS dated at *ca.* 5100 yrs BP. An older basal sediment date of *ca.* 8500 years was found as anticipated for the littoral core NAG30.

Table 4.2: Dating results (Dating Laboratory University Of Helsinki)

NAG27 Lab. no.	**Sample**	$\delta^{13}C$	**AGE (BP)**
Hela-398	NAG27, 29.6 - 30.0 cm	-26.2	1295 ± 70
Hela-399	NAG27, 55.0 - 55.4 cm	-26.6	2260 ± 125
Hela-400	NAG27, 88.6 - 89.0 cm	-27.2	3080 ± 70
Hela-401	NAG27, 133.2 - 133.6 cm	-26.7	3905 ± 95
Hela-402	NAG27, 160.0 - 160.4 cm	-26.6	4945 ± 75
Hela-415	NAG27, 176.0 - 176.6 cm	-26.5	5495 ± 75
NAG30			
Hela-414	NAG30, 119.0 - 120.0 cm	-26.1	5105 ± 120
Hela-413	NAG30, 131.0 - 132.0 cm	-26.6	6375 ± 70
Hela-414	NAG30, 143.0 - 144.0 cm	-27.1	8105 ± 80
Hela-403	NAG30, 154.0 - 155.0 cm	-27.2	8430 ± 80

Table 4.3: Sediment accumulation rates derived from ^{14}C AMS radiocarbon dates

NAG27 Time Period Yrs BP	**Depth (cm)**	**No. of Years**	**Rate of Sediment accumulation cm yr^{-1}**	**Rate of Sediment accumulation yr cm^{-1}**
5495-4945	16.2	550	0.029	33.95
4945-3905	26.8	1040	0.026	38.81
3905-3080	44.6	825	0.054	18.50
3080-2260	33.6	820	0.041	24.40
2260-1295	25.4	965	0.026	37.99
1295-0	30.0	1295	0.023	43.17
NAG30				
8430-8105	11	325	0.033	29.55
8105-6375	12	1730	0.007	144.17
6375-5105	12	1270	0.009	105.83
5105-0	119	5105	0.023	42.90

Uncalibrated ^{14}C AMS radiocarbon years BP is used to calculate sediment accumulation rates for NAG27 (Table 4.3). Linear extrapolation is used to interpolate ages between dates and extrapolate to the top and bottom of the sediment core in TILIA (Grimm, 1991). This constrains interpretation for intervening levels and determination of changes does not account for deviations in accumulation rate. The age-depth profile (Figure 4.21) for Lochnagar (NAG27) is consistent with a slow sedimentation rate throughout the sequence. The average accumulation rate is approximately 0.033 cm yr^{-1} (or 32.8 yr cm^{-1}). Fastest sediment accumulation rates are found around 4000 yrs BP with declining rates in sediments post 3000 yrs BP. In the littoral core

NAG30 a slow rate of sediment accumulation (0.033 cm yr^{-1}) was estimated for the base of the core. The lowest sediment accumulation rates (0.008 cm yr^{-1})) for the CHILL sediments collected from Lochnagar were calculated for the period between 8100-5000 ^{14}C yr BP. This result accords with expected lower rates of accumulation in lake littoral areas.

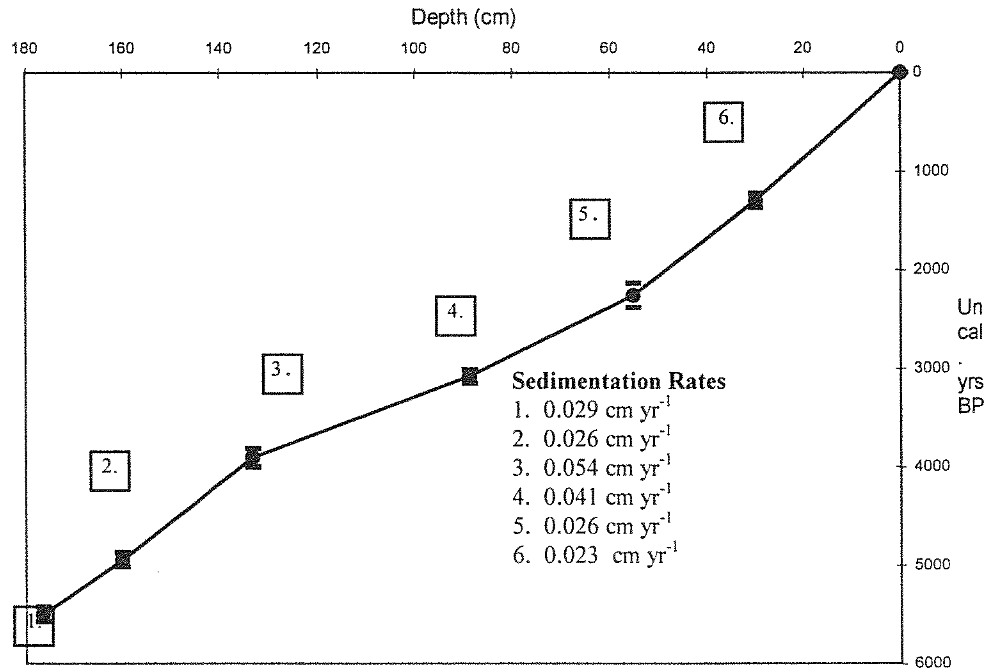


Figure 4.21: Composite age/depth curve for Lochnagar (NAG27)

4.2.2.1 Calibration of AMS ^{14}C Dates

Calibration of the AMS ^{14}C chronology was achieved using the programme CALIB (Stuiver & Reimer, 1993). Age depth models using fixed (weighted) and non-fixed (non-weighted) surface dates were examined and were found to be similar. This gives confidence that the fixed models accurately represent the age-depth and gives the best-calibrated chronology. Weighted models were adopted for both the deepwater and littoral chronologies. This gave a calibrated age sequence of 6250 years BP for the master core NAG27. The littoral core NAG30 spanned 9030 cal yr BP (see Appendix 2).

Core correlation using slot sequencing of LOI and DW results (see section 3.1.1) enabled the calibrated ages for NAG27 to be applied to the appropriate sample in the parallel core NAG28. This enabled calibrated dates to be estimated for sediment lithology and biological reconstructions for analyses conducted on the parallel core. NAG28 was estimated to be slightly younger than NAG27 at *ca.* 5700 cal yr BP.

4.3 Diatom Analysis - C.P. Dalton, University College London

A total of 221 diatom species were identified in 185 samples selected from the Lochnagar master core NAG27. Sixty samples were selected from the lower half of NAG30 (below 90 cm) and 111 species identified. This cut-off point in the littoral core was estimated based on the pollen chronology and samples above this point in time are represented in NAG27. Sample resolution for diatom analysis in NAG27 is estimated to be *ca.* 35 years and for NAG30 *ca.* 60 years and therefore are within the CHILL protocol. Diatom counts were transformed to percentages and taxa with a maximum occurrence of less than 1% and not found in more than two samples were eliminated using TRAN (Juggins, 1994). This reduced the working data set to 146 taxa for NAG27 and 83 taxa for NAG30. Summary diatom diagrams are presented in Figure 4.22 and 4.23. The diatom stratigraphical data are plotted according to sediment depth (cm), AMS radiocarbon dates, calibrated dates with significant zones of change highlighted.

The number of diatom taxa found in each sample in NAG27 typically varies between 22 and 44, and the sample heterogeneity (Hill's diversity index - N2 (Hill, 1973)) for different core depths ranges from 20-40 through the NAG27 core (Figure 4.24). A trend line has been added to Figure 4.24 to give a general impression of change. Generally the pattern of taxa numbers reflects sample heterogeneity through the core, with declines in both in the top 20 cm. High levels of sample heterogeneity are maintained throughout the majority of the core (average N2 = 34). Species diversity declines slightly for the most recent sediments (average N2 = 28). Sample heterogeneity was lower in the littoral core NAG30 with average N2 just 14. Lower species numbers and diversity (N2) was generally found in the littoral core indicating that peripheral lake habitats in these waters are not as diverse as the deepwater sediments where diatoms may have accumulated from multiple aquatic habitats. This result does not conform to expected patterns of higher diversity in littoral habitats. A high degree of mixing due to the exposure of the lake, poorer shallow water diatom preservation or a greater contribution from a uniform local community may all be influencing diatom communities in the lake.

Diatom analysis of the Lochnagar NAG27 core reveals multiple floristic changes (Figure 4.22). *Achnanthes scotica, Tabellaria flocculosa, Achnanthes detha* are present throughout the sequence with fluctuating levels. Species such as *Fragilaria vaucheriae, Aulacoseira lirata* var *alpigena, Navicula schassmannii, Navicula seminuloides* are also present throughout most of the core but are absent in the top 10 cm. These species declines are paralleled with increases in

Achnanthes marginulata, A. [marginulata] f. major and *Eunotia incisa*. Other changes of note include high levels of *Fragilaria virescens* var *exigua* between 150 and 30 cm, and notable expansions of *Eunotia pectinalis* var *undulata* and declines in *A. [marginulata] f. major* above 90 cm.

Diatom assemblages between 90-155 cm in the littoral core NAG30 are illustrated in Figure 4.23. The assemblages in the littoral core and the deepwater core are largely similar to each other, however lower levels in *Tabellaria flocculosa, Fragilaria vaucheriae* and higher levels of *Aulacoseira lirata* and *A. perglabra* are found in the littoral core. Frequently occurring species include *Fragilaria virescens* var *exigua, Achnanthes scotica, Aulacoseira perglabra, A. lirata* var *alpigena, A. distans* var *nirvalis* and *A. lirata*. The main species change of note is a large increase in *Aulacoseira lirata* between 125-145 cm paralleled by declines in other *Aulacoseira* species.

4.3.1 Floristic Zones

The fossil assemblages for both cores were zoned stratigraphically using the programme ZONE where multiple methods are used to identify major zones common to all programmes. From comparison of the results six zones were identified in the fossil diatom data in NAG27 and three zones in NAG30. Comparison with the broken-stick model suggests that these zones are statistically significant. No examination of possible overlap or comparison of the zones between NAG27 and NAG30 will be attempted here, as the influence of the different sedimentary environments was not being examined in this project.

<u>NAG27</u> *Zone 1 (176-154 cm)*

Zone 1 reflects high levels of *Tabellaria flocculosa, Achnanthes detha, Fragilaria vaucheriae, and Navicula schassmannii.* This zone is also characterised by low levels of *Fragilaria virescens* var *exigua*, and increases in *Aulacoseira distans* var *nivalis*.

NAG27 *Zone 2 (153-93 cm)*

Zone 2 is delineated with high levels of *Fragilaria virescens* var *exigua* and *Aulacoseira perglabra.*

NAG27 *Zone 3 (92-46 cm)*

Zone 3 differs from zone 2 with declines in *Aulacoseira lirata* var *alpigena, A. distans* var *nivalis, Navicula schassmannii, Fragilaria capucina* var *gracilis* and large expansions in *Eunotia pectinalis* var *undulata, A. [marginulata] f. major.*

NAG27 *Zone 4 (45-28 cm)*

Zone 4 reflects a decline in *Fragilaria virescens* var *exigua, Aulacoseira lirata* var *alpigena, Navicula schassmannii* and increases in *Achnanthes marginulata, A. minutissima* var *scotica.*

NAG27 *Zone 5 (27-10 cm)*

Zone 5 is delineated with major expansions in *Achnanthes [marginulata]* f. *major, A. marginulata, Eunotia incisa* and *Navicula krasskei*, *Fragilaria vaucheriae* while declines are apparent in *Fragilaria virescens* var *exigua.*

NAG27 *Zone 6 (9-0 cm)*

The uppermost zone (6) is characterised by the virtual disappearance of *Fragilaria vaucheriae, Aulacoseira lirata* var *alpigena, Navicula schassmannii, Navicula seminuloides, Navicula cocconeiformis* and major increases in *Achnanthes marginulata* spp. and *Eunotia incisa.*

NAG30 *Zone a (155-144 cm)*

The basal sediments of NAG30 are characterised by high percentages of *Aulacoseira* species.

NAG30 *Zone b (143-123 cm)*

The onset and sharp expansion of Aulacoseira lirata var lirata represent zone b. This is paralleled by proportional decreases in other *Aulacoseira* species. The diatom assemblages are dominated again primarily by *Aulacoseira* species. Another notable change is the expansion of *Achnanathes [marginulata]* f. *major.*

NAG30 *Zone c (122-90 cm)*

The final zone delineated in NAG30 is characterised by a decline and disappearance of *Aulacoseira lirata* var *lirata* and recovery in *Aulacoseira perglabra* and *A. distans* var *nirvalis.* Expansions in zone *c* of *Fragilaria virescens* var *exigua, Achnanathes marginulata* and *A. austriaca* var *helvetica* are also evident.

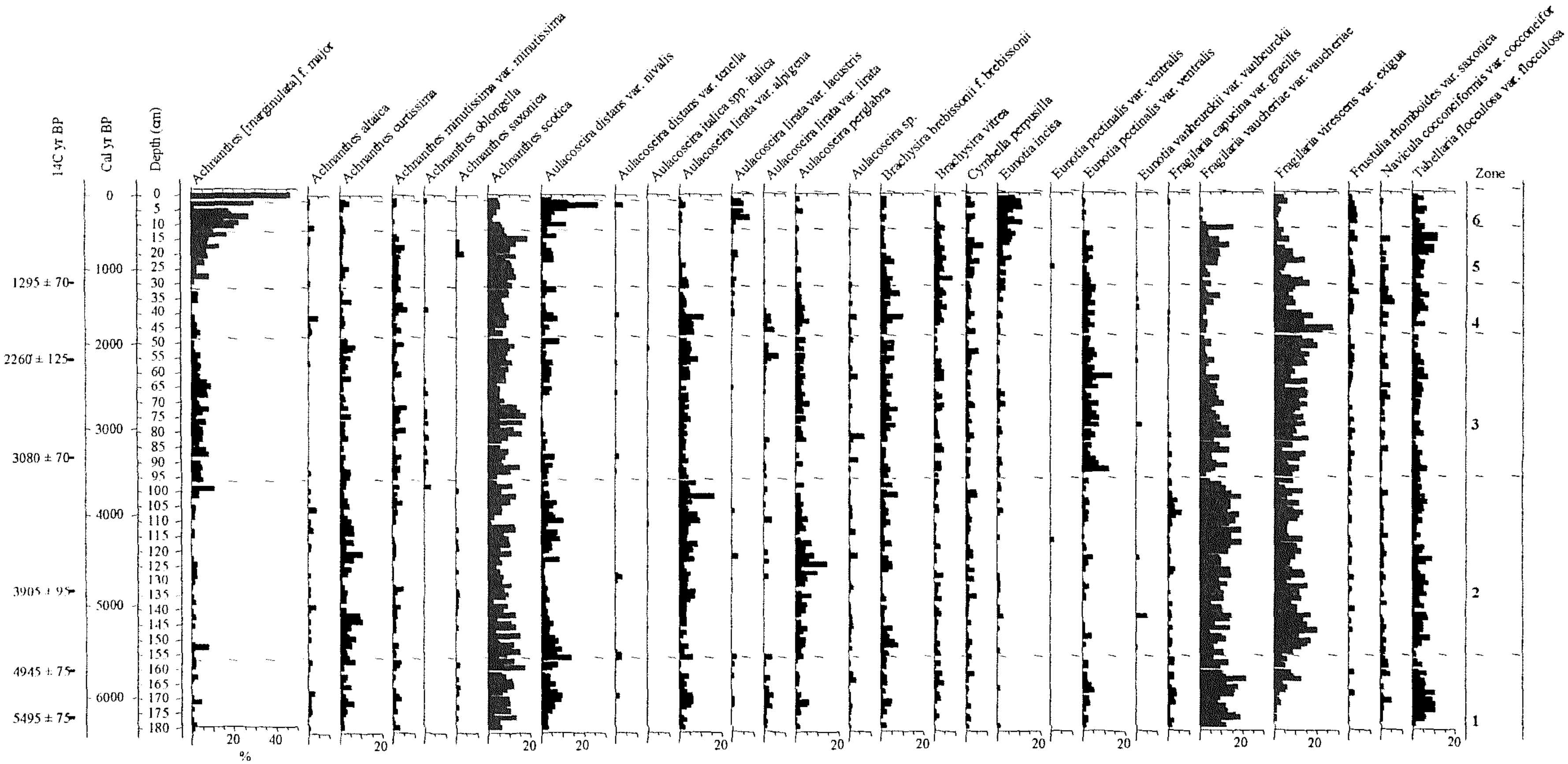


Figure 4.22: Summary Diatom profile (NAG27)

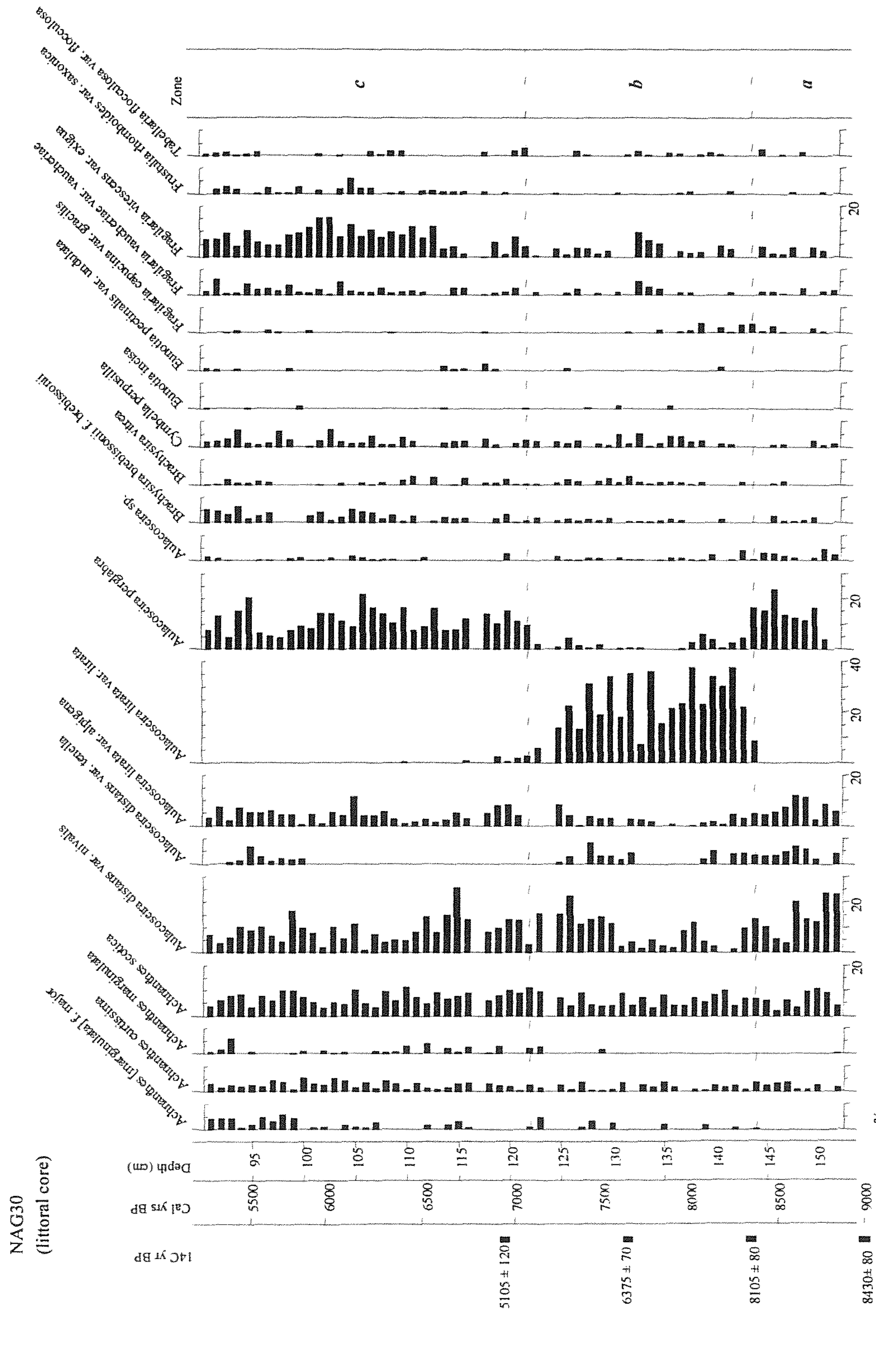


Figure 4.23: Summary Diatom profile (NAG30)

The floristic changes in NAG27 described in zones 1-5 are not reflected in changes in the diversity index (N2). However, between zone 5 and 6 the sharp decline in N2 is clearly a reflection of the notable declines in important species including *Fragilaria virescens* var *exigua, F. vaucheriae, Aulacoseira lirata* var *alpigena, Navicula schassmannii, Navicula seminuloides* and *Navicula cocconeiformis.* A gradual increase in N2 is evident in NAG30. Diversity only reaches levels apparent in NAG27 at this point.

4.3.2 Diatom Concentrations

Diatom concentrations for NAG27 were calculated using the microsphere method (Battarbee & Keen, 1982). The concentration of diatom valves per gram of wet sediment is illustrated in Figure 4.24. Valve concentrations are variable up the core profile. Concentrations are highest at the base of the core with peaks of up to 30 x 10^8 valves g WS^{-1}. A trendline indicates an average valve concentration maximum of 21 x 10^8 valves g WS^{-1} at approximately 140 cm. Above 140 cm the valve concentrations decline steadily. Valve concentrations are maintained around 10 x 10^8 valves g WS^{-1} between 80-40 cm and decline again toward the top of the core. Highest diatom concentrations are found in zone 2 but these decline at the top of the zone. Zone 3 and half of zone 4 corresponds to a period of steady diatom valve concentrations while zones 5 and 6 have the lowest concentrations of the core. The diatom valve concentrations profile is not reflected closely in the profile of any one species. Diatom concentrations in the littoral core (NAG30) were higher than the deepwater core (NAG27).

4.3.3 Diatom Accumulation Rates

Diatom valve concentrations are only indirect proxies for diatom productivity as sediment accumulation rates will not be constant. In order to correct for sediment accumulation rates diatom accumulation rates (DAR cm^{-2} $year^{-1}$) were calculated by multiplying the wet mass accumulation rate (cm^{-2} $year^{-1}$) and the diatom concentration (cells g wet wt^{-1}). The DAR profile for NAG27 (Figure 4.24) is similar to the diatom concentration profile with higher rates at the base of the core and declines toward the top. The DAR rates are highest, suggesting greatest diatom productivity, for the period of highest sediment accumulation in zone 2.

Diatom accumulation rates calculated for the littoral core NAG30 indicate greatest accumulation at the base of the core with sharp declines by 140 cm (Figure 4.24). Accumulation rates remain steady throughout the rest of the core section examined.

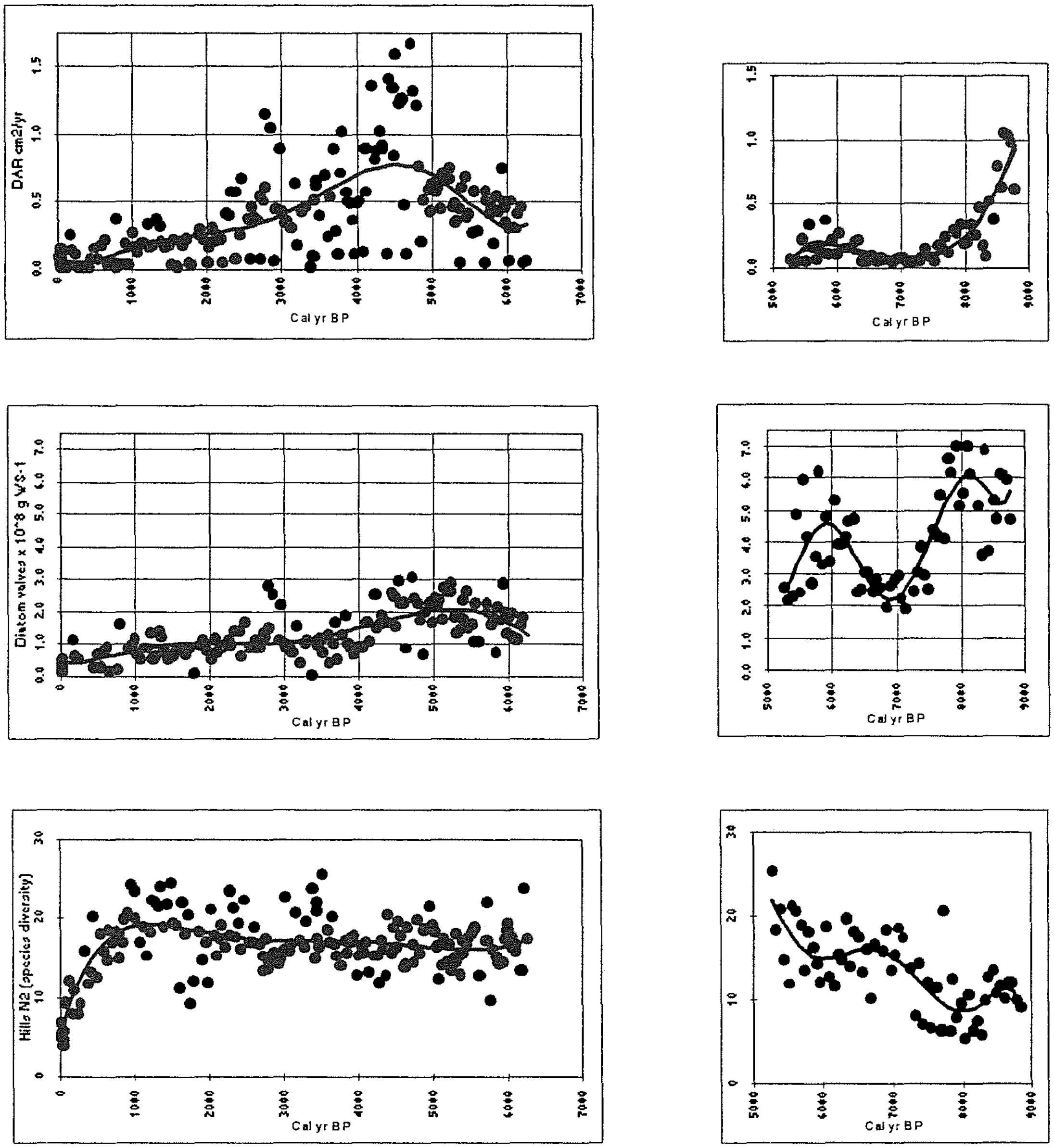


Figure 4.24: Hills diversity Index (N2), Diatom valve concentrations (valves g WS^{-1}) and Diatom accumulation rates (DAR cm^{-2} $year^{-1}$) for the master core NAG27 and the littoral core NAG30.

4.3.4 Ordination Analysis

Ordination analysis is used to illustrate the floristic signal in the master core only (NAG27) by reducing the species variation to a few ordination axes. Changes in ordination sample scores represent variation in species assemblages with depth and thus through time. Ordination of the fossil diatom assemblages using detrended correspondence analysis (DCA) gave an axis 1 and axis 2 gradient of 2.4 and 2.3 SD units respectively, so the data were subjected to linear ordination analysis (PCA) (Table 4.4). The PCA biplot of axes 1 and 2 is represented in Figure

4.25. Zone 6 (10-0 cm) has the most dissimilar assemblages while zones 5-1 have many species in common. PCA axis scores are also represented as TILIAGRAPH profiles in Figure 4.26. PCA axis 1 captures 6.3 % of the variation in the diatom assemblages while axis 2 adds an additional 3.4%. The first four ordination axes represent just 15.4% of the variation in the fossil diatom assemblages.

Table 4.4: Summary statistics for PCA of NAG27 fossil diatom data (n = 185 samples)

Axes	1	2	3	4	Total variance
Eigenvalues	0.063	0.034	0.032	0.025	1
Cumulative percentage variance of species data	6.3	9.7	12.9	15.4	
Sum of all unconstrained eigenvalues					1

4.3.5 pH Reconstruction

The WA-PLS diatom-pH transfer function derived for the AL:PE training set (Cameron *et al.*, 1999) was applied to the fossil assemblages from the Lochnagar cores (NAG27 and NAG30) using WA-PLS Version 1.1 (Juggins & ter Braak, 1996). Inferences for historical pH were obtained by adding core fossil diatom counts from different sediment depths as passive samples to the AL:PE surface sediment calibration samples using the WA-PLS (3) model. The WA-PLS model with two components has an r^2 of 0.80 and RMSEP of 0.34. The optimal number of WA-PLS components to use is based on RMSEP. The modelled relationship between diatoms and pH was used to infer pH levels for the fossil assemblages at different depths in the deepwater and littoral sediment cores.

Eighty-seven percent of the fossil taxa in NAG27 and 94% of the taxa in NAG30 are present in the training-set. Of the 13% of the taxa not present in the training-set the following taxa have high N2: *Diatom mesodon, Fragilaria capucina* var. *gracilis, Achnanthes minutissima* var. *scotia* and *Achnanthes oblongella*. While numbers are low these taxa are influential in the pH reconstruction. The lack of analogues in the modern training-set limits interpretation. Other taxa with high N2 in the training-set and low N2 in the fossil data set include *Cymbella hebridica, Peronia fibula* and *Eunotia tenella*. This suggests that these species have a good response to pH in the modern training-set but this is not been reflected in the fossil data set.

The diatom-pH reconstruction for NAG27 is illustrated in Figure 4.27. Jack-knifed inferred pH for each core sample and their error terms (as determined from the RMSEP of the training-set) are presented in Appendix 3. Diatom inferred pH for the fossil samples gives a fluctuating range between 5.5 and 6.6 throughout the history of the core (Figure 4.27). Zone 1, pre-5000 cal yr BP, was a period of increasing diatom-inferred pH ranging from a basal-low of 6.1. Zone 1 has an average diatom-inferred pH of 6.3. Increasing inferred pH levels at the top of zone 1 reflect increases in *Aulacoseira distans* var *nivalis* and *Fragilaria virescens* var *exigua.* Inferred pH estimates for zone 2 are the highest for the core (maximum 6.6 pH units) and reflect the presence of high levels of *Fragilaria virescens* var *exigua* and *Aulacoseira perglabra.* This period of high pH is dated to between 5500-4200 cal yr BP. Diatom-inferred pH values decline at the top of zone 2 in response to declines in *Aulacoseira distans* var *nivalis, A. perglabra* and *Navicula schassmannii.* Zone 3 reflects lower levels in diatom inferred pH of approximately 5.8 pH units. Further sharp pH declines from *ca.* 6.0 to 5.5 are apparent above 40 cm (*ca.* 1000 cal yr BP). Two obvious areas of change with declines in diatom reconstructed pH are therefore post 4200 cal yr BP and post 1000 cal yr BP. At no other point in the core is there such an obvious change in diatom-reconstructed pH. The post-1000 cal yr BP decrease of diatom-inferred pH is associated with decreases in *Fragilaria virescens* var *exigua, Eunotia pectinalis* var *undulata, Aulacoseira lirata* var *alpigena, Navicula schassmannii* and increases in *Achnanthes marginulata, A. minutissima* var *scotica.* Major increases in acidophilous taxa in the most recent sediments correspond to other studies showing a reduction in pH in the last few hundred years.

WA-PLS diatom reconstructed pH for the littoral core NAG30 is illustrated in Figure 4.27 and indicates inferred levels in the region of pH 6.0-6.5. These levels correspond with the inferred levels for the base of NAG27. This represents the period 5000-9000 cal yr BP. A decline in pH is inferred coincident with expansion of *Aulacoseira lirata* var *lirata.*

4.3.6 Conclusion

In summary, diatom analyses show shifts in assemblages that may correspond to cold/warm phases. A general decline in pH is evident throughout the 9000-year period covered by the Lochnagar sediment cores. A more productive phase is possibly indicated around 5000-4000 cal yr BP with highest diatom concentrations and diatom accumulation rates. This is also reflected in high levels of diatom inferred pH. Two periods of change are evident at 4000 and 1000 cal yr BP. Large declines species diversity and in diatom inferred pH are evident in the last 1000 years.

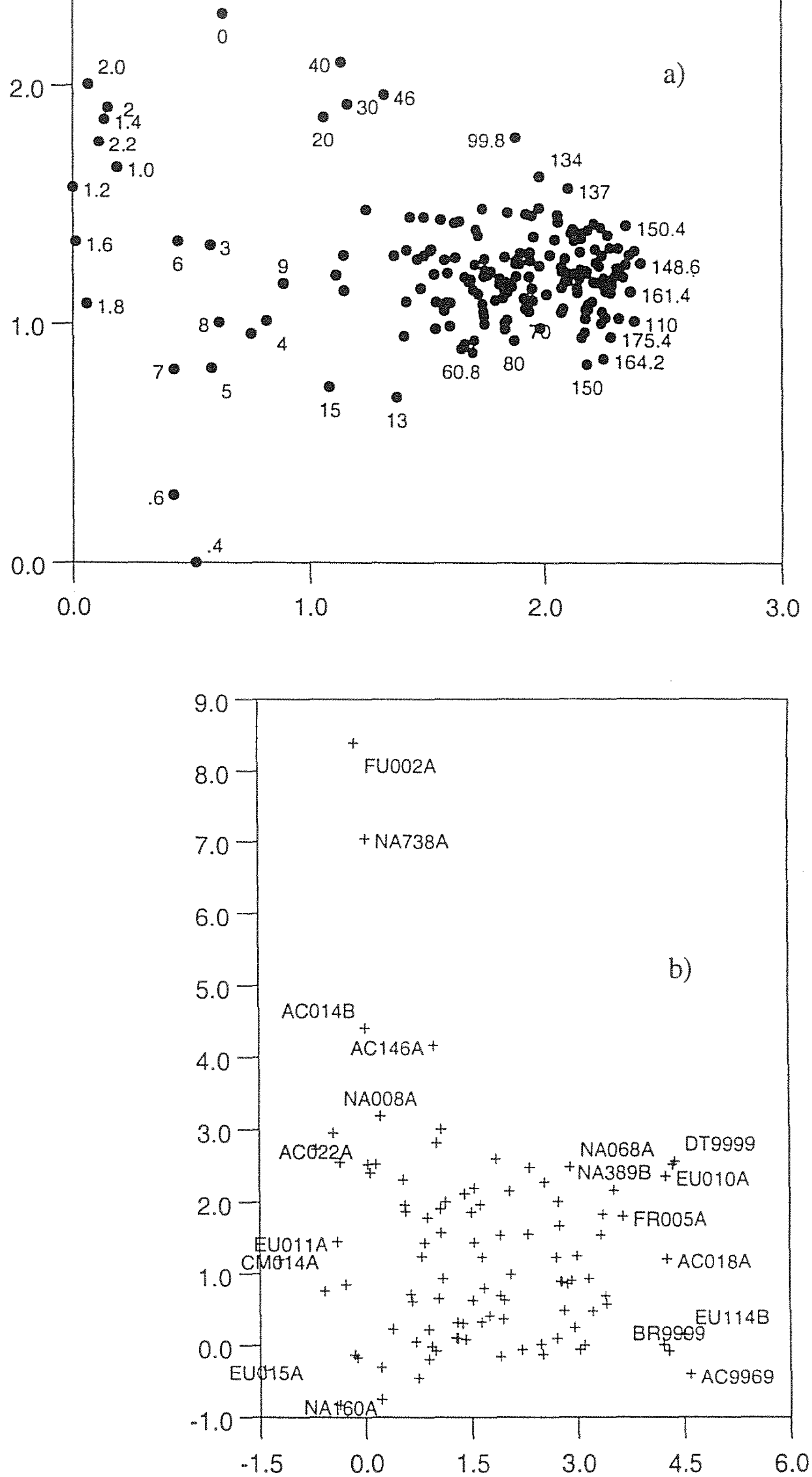


Figure 4.25: PCA biplot of axes 1 and 2 a) sediment samples, b) species (NAG27)

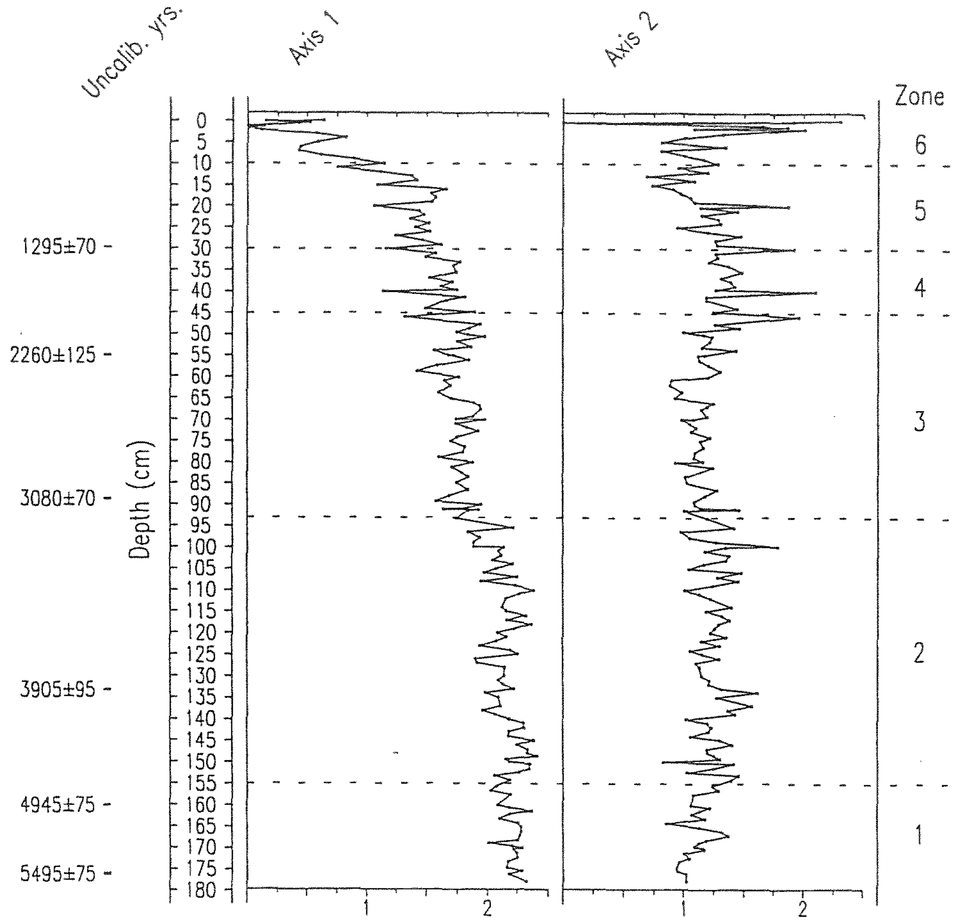


Figure 4.26: PCA axis scores 1 & 2 for NAG27 represented as TILIAGRAPH profiles

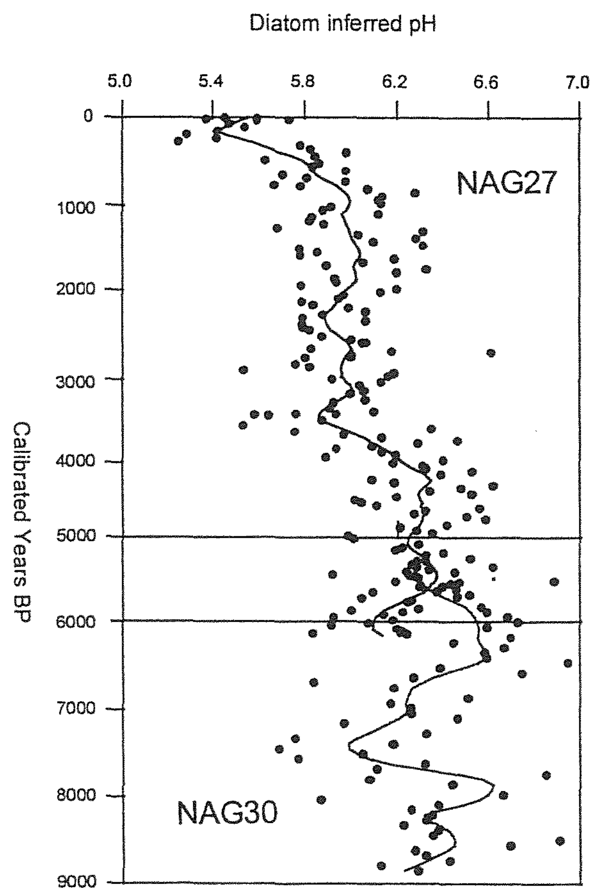


Figure 4.27: Diatom-inferred pH for NAG27 and NAG30 using the AL:PE WA-PLS(3) model

4. 4 Chironomidae analysis - S.J. Brooks, Department of Entomology, The Natural History Museum

The sampling resolution was sufficient to pick up major trends in the chironomid response to environmental change. Four grams of wet sediment were necessary to provide enough material (100-200 head capsules per sample) and samples were therefore bulked over 1 cm.

Chironomid head capsules were in good condition and abundant in NAG28 and NAG30. The results of the chironomid analysis are presented in Figure 4.28. A total of 48 samples was examined from core NAG28 and a further 19 samples from core NAG30. A total of 64 taxa were identified from both cores. Sediments in the core NAG28 covered the period from the present day to approximately 5750 cal yr BP. The core NAG30 covered the period from 5750 to 9000 cal yr BP. Zone boundaries were identified using the computer programme ZONE. The data were compared with a broken stick model, using the program BSTICK (Bennett, 1996), to identify which zone boundaries were statistically significant. Two significant zones were identified in the section examine of the littoral core and five significant zones were identified in the deepwater core (NAG28).

4.4.1 Taxonomic notes

The taxon Tanytarsini 'no spur' comprised tanytarsine specimens in which the mandibles were missing but in which there was no spur present on the antennal pedestal. Most of the specimens assigned to this taxon probably comprised Tanytarsina group B and *Tanytarsus lugens*-group, since these taxa were common in the samples and neither have a spur on the antennal pedestal, but in the absence of mandibles their correct identity could not be confirmed.

NAG30 Zone Nch-1

The zone is dominated by *Corynocera ambigua, Microtendipes* and Tanytarsini 'no spur' which are all present at an abundance >10%. *Micropsectra insignilobus*-group increases abruptly in mid-zone. Nineteen other taxa were also recorded from the zone but all remained below 10% abundance.

NAG30 Zone Nch-2

Corynocera ambigua, Microtendipes, Polypedilum nubeculosum-group and Tanytarsini 'no spur' all show declines in abundance in this zone compared with the previous zone, although *Microtendipes* does recover again towards the end of the zone. Taxa showing major increases in

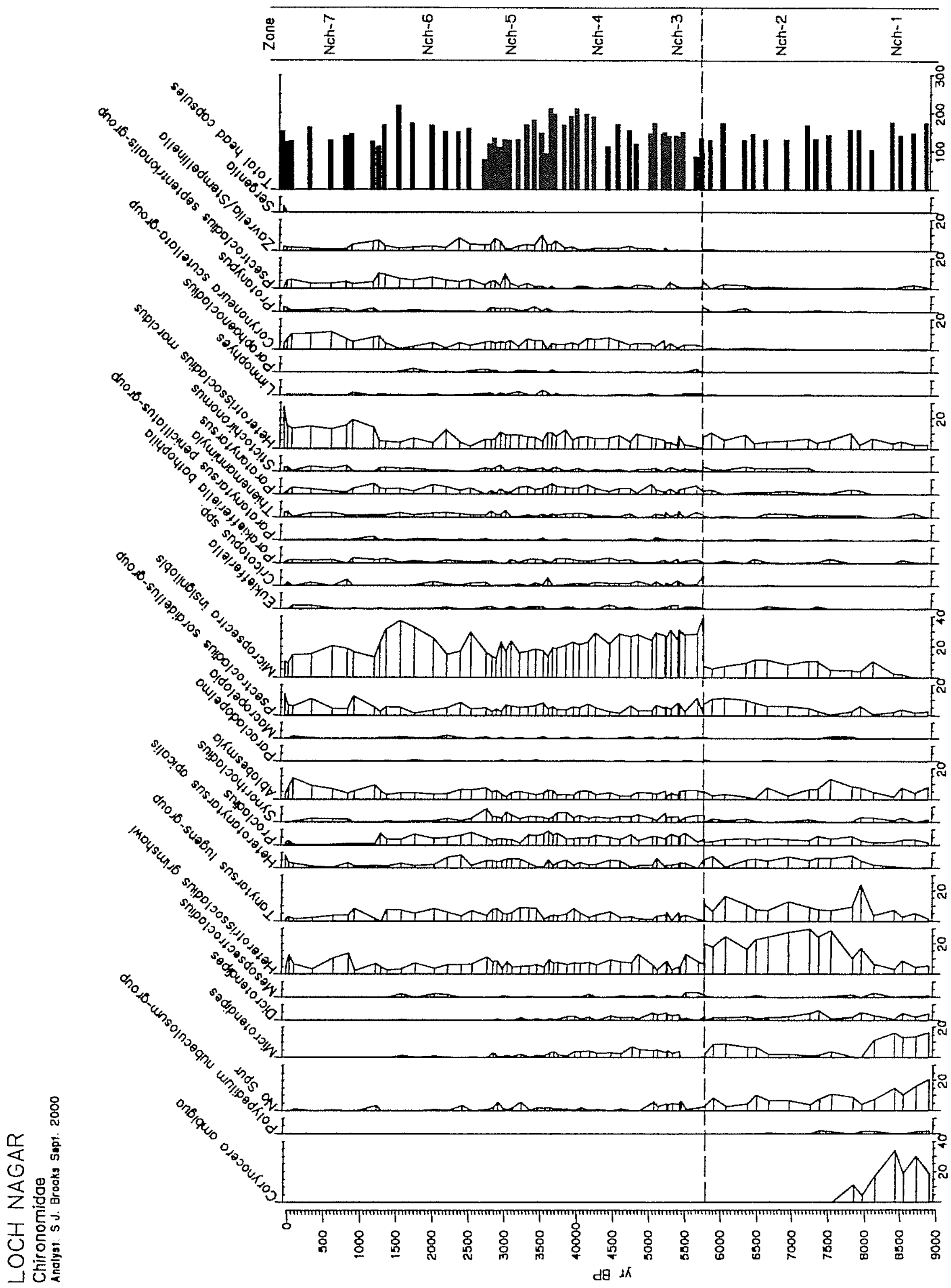


Figure 4.28: Holocene chironomid stratigraphy from Lochnagar. Zones Nch-1 and Nch-2 are from core NAG30 sampled in 4 m of water. Core NAG28 spans zones Nch-3 to Nch-7 and was sampled in 20 m of water.

abundance include *Heterotrissocladius grimshawi, Tanytarsus lugens*-group, *Heterotanytarsus, Psectrocladius sordidellus*-group, *Paratanytarsus* and *Stictochironomus*.

NAG28 Zone Nch-3

This zone is dominated by *Micropsectra insignilobuis*-group. *Microtendipes* and *Dicrotendipes* increase suddenly in mid-zone and *Mesopsectrocladius* declines at the same time.

NAG28 Zone Nch-4

This zone is characterised by declines in Tanytarsini 'no spur' and an increase in *Zavrelia/Stempellinella*.

NAG28 Zone Nch-5

This zone is delineated by declines in *Microtendipes* and *Dicrotendipes* and increased abundance of *Zavrelia, Protanypus, Psectrocladius septentrionalis*-group and *Tanytarsus lugens*-group.

NAG28 Zone Nch-6

Dicrotendipes becomes absent from the fauna in this zone. *Mesopsectrocladius* peaks in mid-zone but disappears from the core by the end of the zone.

NAG28 Zone Nch-7

This zone differs from zone Nch-6 by the absence of *Microtendipes,* lower abundance of *Procladius* and *Micropsectra insignilobus*-group and increased abundance in *Heterotrissocladius grimshawi, Psectrocladius sordidellus*-group, *Corynoneura scutellata*-group, *Ablabesmyia*, and *Heterotrissocladius marcidus*. *Sergentia* appears for the only time in the entire sequence in the two upper samples of the zone. *Heterotrissocladius grimshawi, Heterotanytarsus, Ps. sordidellus*-group and *H. marcidus* also peak in the upper two samples and there are coincidental declines in *Ablabesmyia* and *M. insignilobus*-group.

4.4.2 Ecological interpretation

The changes in the chironomid fauna between zones Nch-1 and Nch-2 in core NAG 30 suggest a response to both changes in temperature and pH (Figure 4.28). Declines in thermophilic taxa like *Polypedilum* and *Microtendipes*, together with increases in cold-water taxa, such as *Heterotrissocladius grimshawi*, *Micropsectra insignilobis* and *Stictochironomus*, suggest temperatures were falling between about 8600 and 7300 cal yr BP. At the same time the rise in *Heterotanytarsus* and *Psectrocladius sordidellus*-group suggests a response to falling pH.

Corynocera ambigua represents up to 40% of the chironomid fauna prior to 8400 cal yr BP, so the elimination of the species from the fauna after about 7800 cal yr BP is particularly significant. The species is often regarded as a cold-stenotherm so its disappearance at a time when changes in other elements of the chironomid fauna suggest lower temperatures is rather surprising. However, work by Brodersen & Lindegaard (1999) has shown that the species may occur in warm (*ca.* 20°C) shallow lakes and that temperature may not be a limiting factor for the species. The species often occurs at high abundance in fossil assemblages but may be eliminated following development of macrophytes, increase in nutrients and oxygen depletion, changes in benthic microalgae production or food availability. If there had been an increase in nutrient concentrations at the time *C. ambigua* disappeared from the fauna LOI values might be expected to rise. However, LOI values actually fall slightly at this time.

Core NAG30 was sampled in 4.2 m of water whereas core NAG28 was sampled in 20.6 m of water. At the point where the two cores overlap (boundary between zone Nch-2 and Nch-3) there are marked differences in the chironomid assemblages reflecting the effect of lake depth on the chironomid fauna. Almost all of the taxa present in the upper samples of NAG30 are also present in the bottom-most samples of NAG28, but their percentage abundance are quite different. For example, *Heterotrissocladius grimshawi, H. marcidus* and *Tanytarsus lugens*-group are more abundant in NAG30 than NAG28 whereas *Procladius, Synorthocladius, Micropsectra insignilobus*-group and *Corynoneura scutellata* are more abundant in NAG28 than NAG30.

In the bottom half of zone Nch-3 (5750-5400 cal yr BP) in NAG28 both *Dicrotendipes* and *Microtendipes* are in very low abundance or absent. Then after 5400 cal yr BP both taxa abruptly increase. Since both taxa are thermophilic it is likely that their absence is in response to a brief cool period.

Declining abundance of *Dicrotendipes* and *Microtendipes* coupled with the rise in *Tanytarsus lugens*-group after 3500 cal yr BP suggests a response to continued decline in temperature. *Dicrotendipes* is eliminated from the fauna after about 2900 cal yr BP and *Microtendipes* after about 1600 cal yr BP suggesting that *Microtendipes* has a lower temperature optimum than *Dicrotendipes*.

The rise in *Zavrelia/Stempellinella* after 5000 cal yr BP suggests the lake may have begun to acidify. A continuing fall in pH from the mid-Holocene is suggested by increases in *Psectrocladius septentrionalis*-group after 3600 cal yr BP. A further sudden fall in pH appears to have occurred after about 1300 cal yr BP when there are sharp increases in acidophilic taxa including *Heterotrissocladius grimshawi, H. marcidus* and *Psectrocladius sordidellus*-group together with a decline in the acidophobe *Micropsectra insignilobus*. These faunistic changes suggest a response to natural acidification of the catchment. The increase in *Sergentia, Heterotanytarsus apicalis, Heterotrissocladius marcidus* and *Psectrocladius sordidellus*-group in the uppermost two samples may be in response to post-industrial acidification.

4.4.3 Statistical analysis

The results of PCA are shown in Figure 4.29 as scatter plots of the axis 1 and axis 2 sample scores. Comparison of the axis 1 plot with diatom-inferred pH shows strong similarities in the shape of the curves. This suggests that pH is the most significant variable in driving the changes in the chironomid assemblage throughout the Holocene. The PCA axis 2 curve appears to reflect the response to temperature.

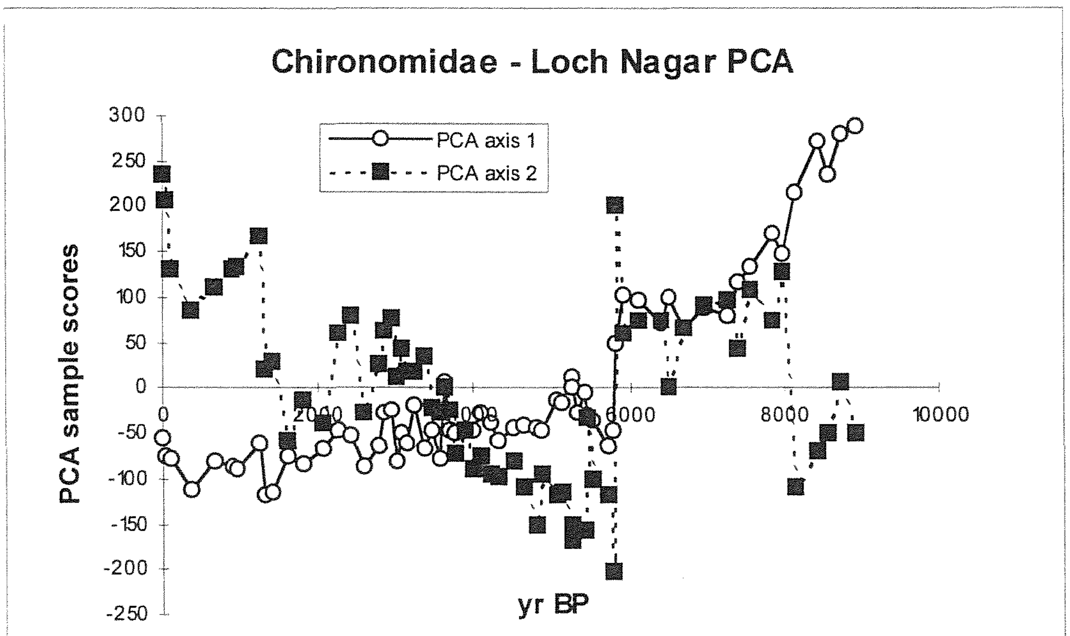


Figure 4.29: PCA axis 1 and axis 2 sample scores. PCA axis 1 appears to reflect a pH signal and axis 2 a temperature signal. The large discontinuity that occurs in both curves at about 5,700 yr BP is the point at which the two cores were merged.

4.4.4 Temperature reconstruction

The chironomid-inferred mean July air temperature for the Holocene ranges between about 10.4°C to 12.2°C (Figure 4.30). The results suggest that Holocene temperatures were at their lowest between 8000-9000 cal yr BP (about 10.5-11.0°C). This was followed by a brief warm period centred on 7600 cal yr BP when temperatures rose to slightly above 12.0°C and *Coynocera ambigua* was eliminated from the fauna. This was apparently the warmest time during the entire Holocene. Temperatures fell again after this to about 11.0°C when *Microtendipes* was less abundant than previously. Between 6500 and 6000 cal yr BP there appears to have been another warm interlude when *Microtendipes* was once more abundant, with temperatures reaching about 11.5°C. This was followed by a brief cold oscillation at about 5700 cal yr BP when both *Microtendipes* and *Dicrotendipes* were virtually absent from the fauna. Between about 5500 and 4500 cal yr BP chironomid-inferred mean July air temperatures once more peaked at about 11.8-12.0°C. There was then a gradual declining trend, reflecting the decrease in abundance of *Microtendipes* and *Dicrotendipes* until about 1500 cal yr BP when temperatures bottomed-out a little below 11°C. Finally from 1500 cal yr BP until the present there was an upward temperature trend. The present day midge-inferred mean July air temperature is about 11.7°C.

Throughout most of the Holocene the temperature curve appears to be driven by the abundance of *Microtendipes* and *Dicrotendipes*. Temperatures are relatively high when the abundance of these taxa is high but chironomid-inferred temperatures decline as these two taxa decline in abundance. The exception to this is at the base of the core when *Microtendipes* and *Dicrotendipes* are both abundant and yet chironomid-inferred temperatures are at there lowest. This is probably due to the influence of *Corynocera ambigua*, which has a relatively low temperature optimum in the calibration set (*ca.* 9.0°C). However, as discussed above, this taxon is not necessarily limited by temperature and it may occur in warm lakes up to 20°C. Therefore, it is possible that the low temperature reconstruction in the early Holocene is incorrect and has been artificially lowered by the high abundance of *Corynocera ambigua*.

4.4.5 Summary

1. The major influence on the chironomid fauna is the progressive acidification of the lake. A response to falling pH is already apparent by 8000 cal yr BP and this trend continues throughout the Holocene. More abrupt declines in pH are indicated at 3600 cal yr BP, 1300 cal yr BP and 100 cal yr BP.

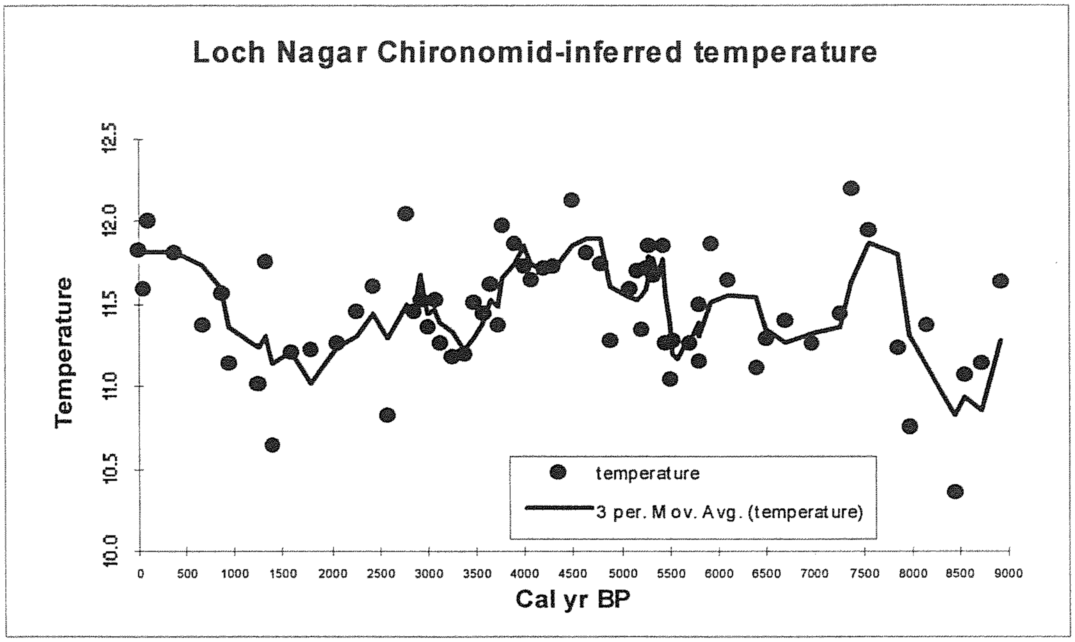


Figure 4.30: Chironomid-inferred Holocene mean July air temperatures at Lochnagar.

2. Fluctuating temperatures are indicated throughout the Holocene with warm periods when chironomid-inferred mean July air temperatures rose above 11.5°C at 7600 cal yr BP, 5700-4000 cal yr BP and 500 cal yr BP to the present. Cool periods during which temperatures fell to about 11°C are indicated at 9000-8000 cal yr BP, 7500-6500 cal yr BP, 5600 cal yr BP, 3500 cal yr BP and 2100-1300 cal yr BP.

3. The depth of water in which the core is taken has an influence on the abundance of head capsules in the sediments but not on the species composition. Nevertheless, this likely to effect the results of the temperature reconstruction.

5. DISCUSSION

This discussion is based on the three biological proxies and the sediment lithology for the Lochnagar lake sediment cores NAG27, NAG28 and NAG30. NAG30 represents the period between approximately 9000-5200 calibrated radiocarbon years and NAG27 represents the period from 6250 cal yr BP to modern day. No attempt will be made to integrate the two chronologies as the interpretations are based on two different lake sedimentation regimes. Where similarities and differences exist, these will be highlighted. A full comparison of chronologies from littoral and benthic sediment regimes would necessitate further work. This work does not fit with the CHILL research agenda but constitutes an interesting research question in itself.

Zonation of the biological data reveals six main areas of environmental change common to all palaelimnological signals. The zones coincide approximately with *(i)* 9000-8500 cal yr BP, *(ii)* 8500-7000 cal yr BP, *(iii)* 7000-5500 cal yr BP, *(iv)* 5500-4000 cal yr BP, *(v)* 4000-1500 cal yr BP and *(vi)* 1500 cal yr BP to present day (see Figure 5.1).

The discussion ends with the main conclusions of the work at Lochnagar.

5.1 Chronology of Lochnagar

5.1.1 *(i)* 9000 - 8500 cal yr BP

The first zone *(i)* from 9000 to 8500 cal yr BP coincident in the pollen and diatom data and is evident at the base of the NAG30 core (Figure 5.1). The pollen assemblage during this time reflects light wood cover, in or near the corrie, of sub-alpine birch scrub, abundant ferns, and some tall herbs growing on fertile brown-earth soils.

No major change was discernible in the sediment lithological parameters (magnetism, particle size, loss on ignition and dry weight). Diatom-inferred pH levels are high with averages of pH 6.3 at the base of the core rising to 6.6 (Figure 5.2). These levels correspond to high diatom valve concentration and high diatom accumulation rates. This is paralleled by a reconstructed response to increasing temperatures and pH in the chironomid data for this early Holocene period (Figure 5.2).

5.1.2 *(ii)* 8500 - 7000 cal yr BP

A second zone *(ii)* in the biological proxies is evident in the pollen, diatom data and chironomid data between 8500 and approximately 7000 cal yr BP. The rise in *Pinus sylvestris* and, a little later, *Alnus glutinosa* pollen *ca.* 8350 cal yr BP reflect the arrival and expansion of these trees in this part of Scotland. Pine stumps occur near the loch and have been dated to 6900 cal yr BP. Early- and mid-Holocene mean summer temperatures must have been about 1.5 - 2°C higher than today to allow this higher altitudinal range.

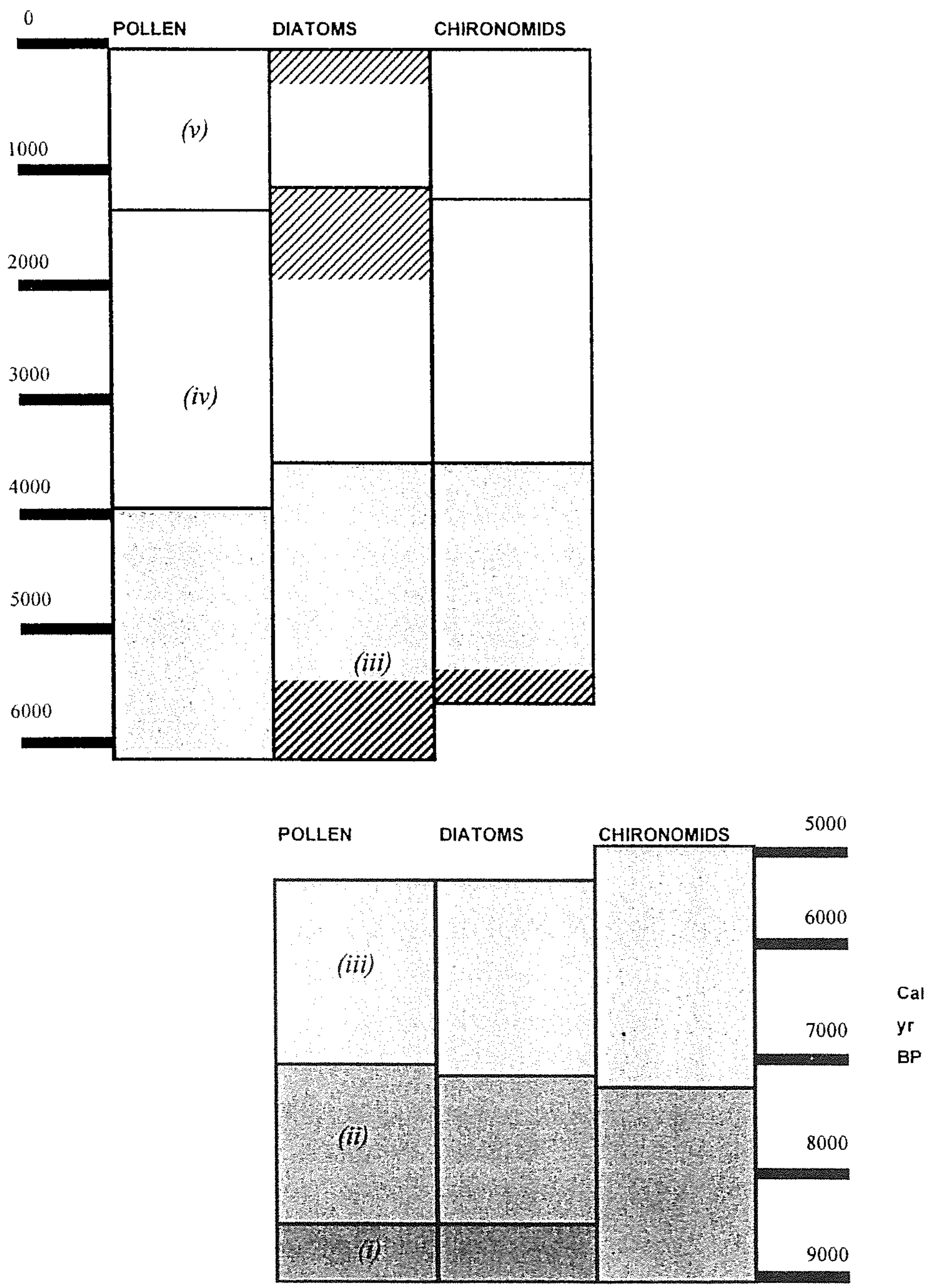


Figure 5.1: Synthesis of biological zones in the Lochnagar sediment cores (NAG27, NAG28 and NAG30) based on Pollen, Diatoms and Chironomids (AMS dates expressed as calibrated years BP).

Sediment lithological measurements from the littoral core again show no change for this period. Diatom inferred pH shows a slight reduction (to pH 6) coincident with an expansion with *Aulacoseira lirata* var *lirata* between 8000 and 7000 cal yr BP. By 7300 cal yr BP chironomid inferred temperatures have stabilised at approximately 11.5°C.

5.1.3 *(iii)* 7000 - 5500 cal yr BP

The period 7000-5500 cal yr BP is represented by zone *(iii)* in NAG30, NAG28 and NAG27. This period straddles the littoral core and the base of the deepwater cores and thus complicates the interpretation because of their different sedimentary environments. The area of overlap (*ca.* 1000 ± 350 cal yr BP) was estimated using pollen chronology and calibrated radiocarbon dates. No comparable trends between cores were visible from the sediment lithology. Between 6200 and 5500 cal yr BP a major decline in % LOI is evident in the master core. This dip in organic matter is one of many and is discussed in more detail in the next zone.

At approximately 120 cm depth in NAG30 and shortly after the base of NAG27 a marked decline in *Ulmus* pollen percentages is apparent *ca.* 6000-6500 cal yr BP and presumably reflects the widespread mid-Holocene decrease of *Ulmus* pollen.

A fluctuating trend in diatom inferred pH is notable for this period. The inferred levels for the littoral core are higher than in NAG27 however the offset is not interpretable without further examination of the littoral and benthic diatom response in this system. The results of chironomid analyses show marked difference in species percentages between the littoral and deepwater cores but similar species. Chironomid inferred temperatures, however, are similar in both the littoral and deepwater cores for this period.

5.1.4 *(iv)* 5500 - 4000 cal yr BP

Rises in Gramineae, *Urtica, Plantago lanceolata* and other herbs indicate human influence between 6250 and 4000 cal yr BP. Increasing Ericaceous dwarf shrubs including *Calluna* and *Vaccinium* and a decrease in woodland indicate the development of grassland and heath with some grazing.

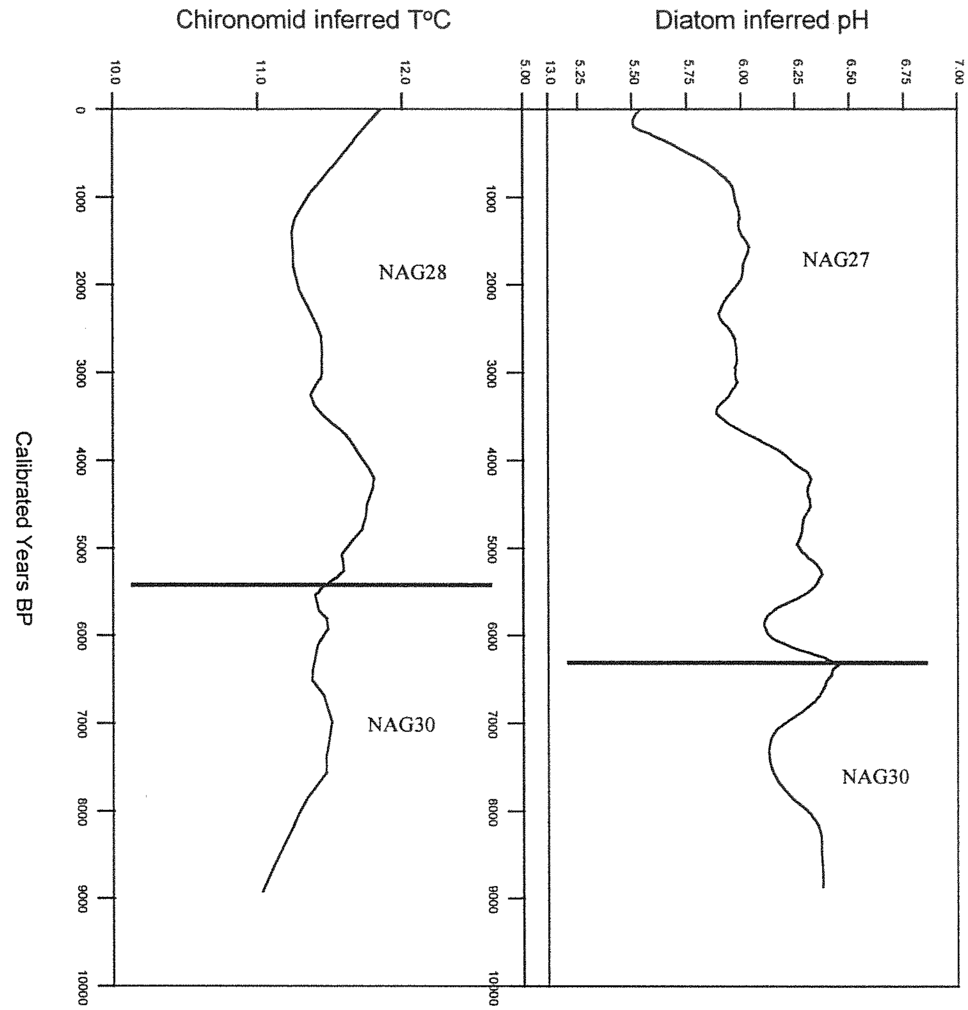


Figure 5.2: Diatom-pH and Chironomid-July temperature Holocene reconstructions at Lochnagar

This zone *(iv)* is delineated by change in the diatom and chironomid assemblages (Figure 5.1). A high diatom inferred pH coincides with highest diatom valve concentration and diatom accumulation rates suggesting higher lake productivity for the period. The high pH levels appear to be associated with declines in *Fragilaria virescens* and *Aulacoseira distans* var *nivalis* rather than increases in more alkaliphilous species. This period has low abundance of chironomidae *Dicrotendipes, Microtendipes* and *Heterotrissocladius marcidus*. The presence of these taxa suggests prevailing warm temperate climatic conditions and thus supports a link between higher diatom inferred pH and warmer temperatures. No consistent link, however, could be established with biomarker indicators for increases in lake productivity for this time.

The core sediment lithology shows three major peaks and three troughs in organic matter between 6200 and 3500 cal yr BP. These periodicity's are based on approximately 1,000 year cycles and may result from a minerogenic inwash from the catchment. A positive relationship between warmer conditions and increases in organic matter could be explained by longer growing seasons. The period of high diatom-inferred pH (and possibly warmer temperature) *ca.* 4000-5000 cal yr BP corresponds to both troughs and peaks in organic matter and dry weight. Thus there is no evidence for systematic variation in the biological proxies or inferred pH linked to DW and LOI. In contrast, results from other lakes (Monteith unpublished) and Lochan Uaine suggest that lake productivity may be enhanced by colder rather than warmer conditions.

Nitrogen and organic carbon content tends to follow the trend of that for loss on ignition. Carbon/nitrogen ratios are constant for the period with an average of about 15. The sequence shows small variations in $\delta^{13}C_{TOC}$ with an amplitude of less than $3^0/_{00}$ (-26.3 to $-23.4^0/_{00}$).

5.1.5 *(v)* 4000 - 1500 cal yr BP

The period is represented by change in the pollen, diatom and chironomid fossil signals.

Further increases in herbs, dwarf shrubs and *Pteridium* in conjunction with decreases in land pollen and spores of tree and shrub taxa to less than 50% of total land pollen and spores - indicate loss of woodland and scrub and local and regional expansion of grassland, moorland and blanket bog. Peat is local at high altitudes today in the Cairngorms (max. elevation *ca.* 1,000 m) and many are extensively eroded.

A decline in inferred pH is evident between 4100 - 3500 cal yr BP. Changes in diatoms include declines in *Aulacoseira lirata* var *alpigena, Fragilaria capucina* var *gracilis* and expansions in *Eunotia pectinalis* var *undulata* and *A. [marginulata] f. major.* Towards the top of this section there is also a decline in *Fragilaria virescens* var *exigua* and *Aulacoseira lirata* var *alpigena.* A period of steady diatom inferred pH levels (*ca.* pH 5.8) are indicated for 3000-1500 cal yr BP. Diatom accumulation rates and diatom concentrations decline.

The chironomidae profile is delineated by declines in *Microtendipes* and *Dicrotendipes* and increased abundance of *Zavrelia*, *Protanypus*, *Psectrocladius septentrionalis*-group and *Stictochironomus*. This suggests that the climate was probably cooler than in the previous zone. A response to temperature change moving from warm to cool is indicated in chironomid data.

Highest levels of dry matter, coincident with the lowest levels of organic matter suggest a major catchment minerogenic input around 3200 cal yrs BP. This is reflected in a peak in particle size measurements. The heaviest $\delta^{13}C_{TOC}$ values also occur around this time coinciding with low organic carbon content. Once again these major lithological changes are not reflected in the biological proxy data or in diatom-inferred pH levels. Declines in diatom valve concentrations and accumulation rates are apparent but these do not recover with increases in organic input for the remainder of the sequence. This major peak in DW probably represents the first effects of anthropogenic disturbance (deforestation) in the catchment. The increase in organic matter post-3000 cal yr BP and increase in the frequency of oscillations (with approximately 10 peaks in organic matter) coincides with paludification of soils and local and regional development of blanket peat. No links between diatom proxy signals sedimentological proxies were found for another high altitude Caringorm lake Lochan Uaine (Barber *et al.*, 1999). The question that needs to be clarified is if these oscillations are associated with catchment disturbance or with climate induced periodicity's. The evidence to date provides no unambiguous support for either of these hypotheses.

5.1.6 *(vi)* 1500 cal yr BP to present day

The final period of major environmental change is evident in the last 1500 years. In the pollen profile further increases in Calluna pollen and also *Sphagnum* represent the development of heath on drier soils and bogs in wetter parts of the Lochnagar catchment area.

The sediment lithology for the more recent sediments is characterised by a number of changes. Further periodicity's in organic matter of 250-350 years appear in the last 1500 years and are similar to trends found at other Cairngorm sites. Carbon/nitrogen ratios also show large variation in the uppermost sediment. High values in %LOI, a decrease in particle size measurements and increases in magnetism are evident. Possible causes of changes in the magnetic properties include an increase in atmospheric pollution particles, dissolution effects or a catchment erosion effect.

This section of the core is delineated with expansions in acidophilous species *Achnanthes [marginulata]* f. *major, A. marginulata, Eunotia incisa, Navicula krasskei, Fragilaria vaucheriae* and declines in circumneutral *Fragilaria virescens* var *exigua.* The uppermost 10 cm is characterised by the virtual disappearance of indifferent taxa *Fragilaria vaucheriae, Aulacoseira lirata* var *alpigena, Navicula schassmannii, Navicula seminuloides, Navicula cocconeiformis* and major increases in acidophilous *Achnanthes marginulata* spp. and *Eunotia incisa.* A decline in pH of up to 0.5 unit is inferred for the top 30 centimetres (1200 cal yr BP). This coincides with further declines in diatom concentrations and N2 (Hills diversity index). This decline in diatom inferred pH is coincident with an increase in magnetic particles in the uppermost sediments post 1000 cal yr BP. Recent industrial acidification in the last 200 years is also evident in the most recent sediments (5 cm) with further large increases in *Achnanthes marginulata* species. The diatom model overestimates pH at 5.7 units for the top 1 cm compared to a measured pH of 5.4.

This period is marked by declines in chironomid genera *Microtendipes*, *Mesopsectrocladius*, *Procladius*, *Micropsectra insignilobus*-group and increases in *Heterotrissocladius grimshawi*, *Psectrocladius sordidellus*-group, *Corynoneura scutellata*-group, *Ablabesmyia*, and *Heterotrissocladius marcidus*. These faunal changes suggest a response to natural acidification of the catchment. An increase in *Sergentia, Heterotanytarsus apicalis, Heterotrissocladius marcidus* and *Psectrocladius sordidellus*-group in the uppermost sample may be in response to post-industrial acidification.

5.2 Conclusions

1) The major pattern of long-term change in the fossil pollen data is a progressive loss of woodland cover and soil deterioration from brown-earths to podsols and shallow peat. The pollen stratigraphy, as interpreted here as reflecting primarily regional and extra-regional pollen deposition, provides no unambiguous evidence for climatic change in the Holocene.

2) The highly distinctive cycles in LOI during the last 6000 years were reflected in bulk and lipid geochemical analysis. However no variation in the biological data was found coincident with these cycles. Further work (e.g. high resolution diatom analysis associated with these cycles) is needed if a direct link with Holocene environmental change is to be established.

3) Particle size was used here to validate palaeoclimate change in biology and to ascertain if there were more extreme events in the early Holocene or any part thereof. Little evidence was found to reflect extreme events in the Holocene sequence. It is concluded that there is limited catchment input but some large grains are getting into the lake sediments here compared to other high altitude sites. This is assumed to be a terrestrial diatom component inwashed to the lake.

4) Magnetic levels at Lochnagar are very low. Levels were slightly higher in the deepwater core compared to the littoral core. Increases in the last 1000 years are assumed to be related to an increase in atmospheric pollution particles, dissolution effects or a catchment erosion effect.

5) Biomarker studies have succeeded in quantifying the relative proportions of autochthonous and allochthonous organic matter in the Lochnagar sediments. The sediments appear to be

dominated by organic matter of terrestrial origin. Short chain *n*-alkanes, methyl-sterols and chlorins indicative of microalgal production have been isolated. These biomarkers are expected to provide information on lake productivity and thus a more direct link with palaeoclimate.

6) Diatom analyses show a general decline in pH throughout the 9000 year period covered by the Lochnagar sediment cores. Highest levels of diatom inferred pH was found in the littoral core. The period around 5000-4000 cal yr BP possibly indicates a more productive period. Large declines species diversity and in diatom inferred pH are evident in the last 1500 years.

7) The major influence on the chironomid fauna is the progressive acidification of the lake. Chironomid inferred temperatures fluctuate through the Holocene at Lochnagar with warm periods when chironomid-inferred mean July air temperatures rose above 11.5°C and cool periods during which temperatures fell to about 11°C.

8) The difference in lake sedimentation and water depth has an influence on the abundance of chironomid head capsules but not on the species composition. No differences were found in the species composition of the diatom assemblages however some differences were apparent in species proportions, diversity, valve concentrations and accumulation rates. These factors are likely to affect the results of the Holocene temperature and pH reconstructions.

9) The retrieval of a benthic and littoral core to achieve the full Holocene record presented difficulties in the research at Lochnagar in terms of linking the chronologies of different proxy data. Future work at Lochnagar could incorporate a fuller comparison of the response to change in the shallow and deepwater environments. A comparison may reveal greater amplitude of different climate signals in different parts of the lake.

10) The highly distinctive results from Lochnagar remain an interesting phenomenon. The potential of these high altitude lake sites as high-resolution sensors of environmental change has been realised in some proxies but not in others. Further comparative work (e.g. with another Cairngorm site Lochan Uaine) could enable the realisation of the potential more fully.

6. References

Barber, K.E., Battarbee, R.W., Brooks, S., Eglinton, G., Haworth, E.Y., Oldfield, F., Stevenson, A.C., Thompson, R., Appleby, P.G., Austin, W.N., Cameron, N.G., Ficken, K.J., Golding, P., Harkness, D.D., Holmes, J., Hutchinson, R., Lishman, J.P., Maddy, D., Pinder, L.C.V., Rose, N. & Stoneman, R. (1999) Proxy records of climate change in the UK over the last two millennia: documented change and sedimentary records from lakes and bogs. *Journal of the Geological Society, London*, **156**, 369-380.

Battarbee, R.W. (1986). Diatom Analysis. In *Handbook of Holocene Palaeoecology and Palaeohydrology* (ed. B.E. Berglund). John Wiley & Sons Ltd UK, pp. 527-569.

Battarbee R.W. & Keen, M. (1982). The use of electronically counted microspheres in absolute diatom analysis. *Limnology & Oceanography* **27**, 182-188.

Bennett, K.D. (1996a). Determination of the number of zones in a biostratigraphical sequence. *New Phytologist* **132**, 155-170.

Bennett, K.D. (1996b). Late-Quaternary vegetation dynamics of the Cairngorms. *Botanical Journal of Scotland* **48**, 51-63.

Berglund. B.E. & Ralska-Jasiewiczowa, M. (1986). Pollen analysis and pollen diagrams. In *Handbook of Holocene Palaeoecology and Palaeohydrology* (ed. B.E. Berglund), J. Wiley, Chichester pp.455-484.

Birks, H.J.B. (1973). *Past and present vegetation of the Isle of Skye - A palaeoecological study.* Cambridge University Press, London, 415 pp.

Birks, H.J.B. (1996). Palaeoecological studies in the Cairngorms - Summary and Future Research Needs. *Botanical Journal of Scotland* **48**, 117-126.

Birks, H.J.B. & Gordon, A.D. (1985). *Numerical methods in Quaternary pollen analysis.* Academic Press, London, 317 pp.

Brodersen, K.P. & Lindegaard, P. (1999). Mass occurrence and sporadic distribution of *Corynocera ambigua* Zetterstedt (Diptera, Chironomidae) in Danish lakes. Neo- and palaeolimnollgical records. *Journal of Paleolimnology* 22, 41-52.

Cameron, N. G., H. J. B. Birks, V. J. Jones, F. Berge, J. Catalan, R. J. Flower, J. Garcia, B. Kawecka, K.A. Koinig, A. Marchetto, P. Sánchez-Castillo, R. Schmidt, M. Šiško, N. Solovieva, E. Štefkovál & M. Toro (1999). Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE Project) and their comparison with the Surface Waters Acidification Programme (SWAP) calibration set. *Journal of Paleolimnology*, **22**, 291-317.

Chambers, J.W.. & Cameron, N.G. (2001) A rod-less piston-corer for lake sediments: an improved, rope-operated hammer corer. *Journal of Paleolimnology* **25** (1), 117-122.

Clark, R.M. & Thompson, R. (1984) Statistical comparison of palaeomagnetic directional records from lake sediments. *Geophysical Journal, Royal Astronomical Society* **76** (2), 337-368.

Cranwell, P. A. (1974). Monocarboxylic acids in lake sediments: indicators derived from terrestrial and aquatic biota, of palaeoenvironmental trophic levels. *Chemical Geology* **14**, 1-14.

Grimm, E.C. (1991). TILIA Version 1.1 & TILIA GRAPH Version 1.19 & 2.0 (unpublished programme).

Heiri, O., Lotter, A.F. & Lemcke, G. (2001). Loss on ignition as a mehtod for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* **25** (1), 101-110.

Hill, M.O. (1973). Diversity and evenness: a unifying notation and its consequences. *Ecology* **54**, 427-432.

Jeffrey, S. W. & Humphrey, G. F. (1975). New spectrophotometric equations for determining chlorophylls a, b, c_1 and c_2 in higher plants, algae and natural phytoplankton. *Biochem. Physiol.* Pflanz. **167**, 191-194.

Juggins, S. (1994). TRAN version 1.7 user manual. Unpublished Programme.

Legendre, P. & Legendre, L. (1998). *Numerical Ecology*. Elsevier, Amsterdam, 853 pp.

Meyers, P. A. & Ishiwatari, R. (1993). Lacustrine organic geochemistry - an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry* **20** (7), 867-900.

McVean, D.N. & Ratcliffe, D.A. (1962). *Plant communities of the Scottish Highlands*. HMSO, London, 445 pp.

Nishimura, M. (1977). Origin of stanols in young lacustrine sediments. *Nature* **270**, 711-712.

Patrick, S. (1997). Measuring and modelling the dynamic response of remote mountain lake ecosystems of environmental change: an introduction to the MOLAR project. European Conference on Environmental and Societal change in Mountain Regions, University of Oxford, December 1997.

Quaternary Isotope Laboratory (2000). CALIB: Radiocarbon Calibration Programme Rev. 4.2. University of Washington.

Rapson, S.C. (1985). Minimum age of corrie moraine ridges in the Cairngorm Mountains, Scotland. *Boreas* **14**, 155-159.

Renberg. I. (1990) A procedure for preparing large sets of diatom slides from sediment cores. *Journal of Paleolimnology* **4**(1), 87-90.

Robinson, N., Eglinton, G., Brassell, S. C., (1984). Dinoflagellate origin for sedimentary 4^{a}-methylsteroids and 5^{a}(H)-stanols. *Nature* **308**, 439-441.

Rose, N.L., Golding, P.N.E. & Battarbee, R.W. (1996). Selective concentration and enumeration of tephra shards from lake sediment cores. *The Holocene*, **6**, 243-246.

Rose N. L., Monteith D. T., Curtis C., Cameron N. G., Patrick S. T., Yang, H, (1998). ECRC Research at Lochnagar 1997/8. Environmental Change Research Centre, Research Report No. 47.

Stuiver, M., and Reimer, P. J., (1993) Extended 14C database and revised CALIB radiocarbon calibration program. *Radiocarbon* **35**, 215-230.

Sugita, S. (1994). Pollen representation of vegetation in Quaternary sediments: theory and method in patchy vegetation. *Journal of Ecology* **82**, 881-897

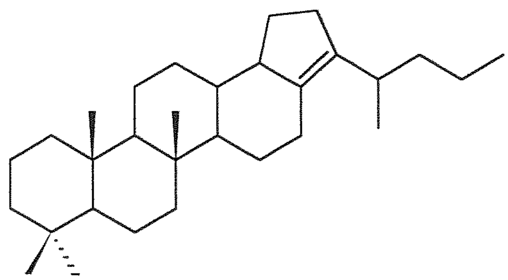
Volkman, J. K., Barrett, S. M., Dunstan, G. A., Jeffrey, S. W. (1993). *Organic Geochemistry* **20** (1), 7-15.

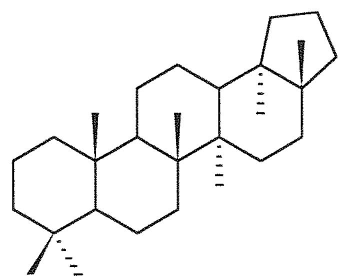
Wathne, B.M., Patrick, S.T., Monteith, D.T. & Barth, H. (1995). *Acidification of Mountain Lakes: Palaeolimnology and Ecology (AL:PE)*. Report for Contract No STEP-CT90-0079. Brussels: European Commission.

Wünsche, L., Mendoza Y. A., Gülaçar, F. O. (1987). *Organic Geochemistry* **13**, 1131-1143.

Xie, S., Nott, C. J., Avsejs, L. A., Volders, F., Maddy, D., Chambers, F. M., Gledhill, A., Carter, J. F., Evershed, R. P., (2000). Palaeoclimate records in compound specific dD values of a lipid biomarker in ombrotrophic peat. Organic Geochemistry, **31** (10), 1053-1057.

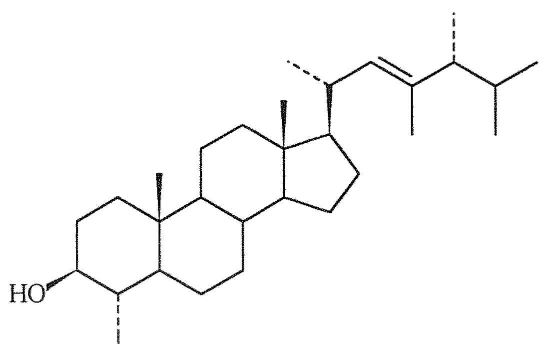
Appendix 1: Sediment Geochemistry





Hop-17(21)ene

17^{b}(H)-22, 29, 30 Trisnorhopane



Dinosterol (4^{a},23,24-trimethylcholest-22-en-3^{b}-ol)

Apppendix 2: Age Depth Model (fixed) ages for NAG27, NAG28 and NAG30

NAG27			NAG28		NAG30		
Depth (cm)	Age (Cal yrs BP)	Standard deviation	Depth (cm)	Age (Cal yrs BP)	Depth (cm)	Age (Cal yrs BP)	Standard deviation
0.00	-48.00	5.03	0	0	0.00	-51.41	78.33
1.00	-16.10	7.52	4	47.68	1.00	-7.39	80.53
2.00	26.42	10.84	8	111.45	2.00	51.30	83.45
3.00	68.94	14.16	12	365.98	3.00	110.00	86.38
4.00	111.45	17.48	16	660.98	4.00	168.69	89.30
5.00	153.94	20.80	20	869.59	5.00	227.39	92.23
6.00	196.41	24.13	24	952.4	6.00	286.08	95.15
7.00	238.86	27.45	28	1238.74	7.00	344.78	98.08
8.00	281.27	30.77	30	1319.44	8.00	403.47	101.00
9.00	323.66	34.09	32	1399.61	9.00	462.17	103.93
10.00	366.00	37.41	36	1597.75	10.00	520.86	106.86
11.00	408.30	40.73	40	1792.52	11.00	579.56	109.78
12.00	450.56	44.05	44	2059.68	12.00	638.25	112.71
13.00	492.76	47.38	48	2246.36	13.00	696.95	115.63
14.00	534.91	50.70	52	2429.69	14.00	755.64	118.56
15.00	577.00	54.02	56	2574.11	15.00	814.34	121.48
16.00	619.03	57.34	60	2787.31	16.00	873.03	124.41
17.00	660.98	60.66	64	2857.6	17.00	931.73	127.33
18.00	702.87	63.98	68	2927.46	18.00	990.43	130.26
19.00	744.67	67.31	72	2996.94	19.00	1049.12	133.18
20.00	786.40	70.63	76	3066.08	20.00	1107.82	136.11
21.00	828.04	73.95	80	3134.87	21.00	1166.51	139.03
22.00	869.59	77.27	84	3248.8	22.00	1225.21	141.96
23.00	911.04	80.59	88	3373.27	23.00	1283.90	144.89
24.00	952.40	83.91	92	3474.43	24.00	1342.60	147.81
25.00	993.65	87.23	96	3575.05	25.00	1401.29	150.74
26.00	1034.79	90.56	98	3641.85	26.00	1459.99	153.66
27.00	1075.82	93.88	100	3708.39	27.00	1518.68	156.59
28.00	1116.74	97.20	104	3758.25	28.00	1577.38	159.51
29.00	1157.53	100.52	108	3890.59	29.00	1636.07	162.44
30.00	1198.20	103.79	112	3989.4	30.00	1694.77	165.36
31.00	1238.74	106.82	116	4071.5	31.00	1753.46	168.29
32.00	1279.16	109.85	120	4202.44	32.00	1812.16	171.21
33.00	1319.44	112.88	124	4300.35	33.00	1870.85	174.14
34.00	1359.59	115.92	128	4495.62	34.00	1929.55	177.06
35.00	1399.61	118.95	132	4636.34	35.00	1988.24	179.99
36.00	1439.50	121.98	136	4787.75	36.00	2046.94	182.92
37.00	1479.26	125.02	140	4885.08	37.00	2105.63	185.84
38.00	1518.89	128.05	144	5079.8	38.00	2164.33	188.77
39.00	1558.39	131.08	148	5144.73	39.00	2223.02	191.69
40.00	1597.75	134.12	152	5258.38	40.00	2281.72	194.62
41.00	1636.99	137.15	154	5274.62	41.00	2340.41	197.54
42.00	1676.09	140.18	156	5339.58	42.00	2399.11	200.47
43.00	1715.05	143.22	158	5437.05	43.00	2457.80	203.39
44.00	1753.88	146.25	160	5458.71	44.00	2516.50	206.32
45.00	1792.58	149.28	164	5534.54	45.00	2575.19	209.24
46.00	1831.15	152.32	168	5713.35	46.00	2633.89	212.17
47.00	1869.57	155.35	170	5794.65	47.00	2692.58	215.09
48.00	1907.87	158.38			48.00	2751.28	218.02
49.00	1946.02	161.42			49.00	2809.97	220.94
50.00	1984.05	164.45			50.00	2868.67	223.87
51.00	2021.93	167.48			51.00	2927.36	226.80
52.00	2059.68	170.52			52.00	2986.06	229.72
53.00	2097.29	173.55			53.00	3044.75	232.65
54.00	2134.76	176.58			54.00	3103.45	235.57
55.00	2172.10	179.62			55.00	3162.14	238.50
56.00	2209.30	180.35			56.00	3220.84	241.42
57.00	2246.36	180.52			57.00	3279.53	244.35
58.00	2283.28	180.68			58.00	3338.23	247.27
59.00	2320.08	180.84			59.00	3396.92	250.20
60.00	2356.74	181.00			60.00	3455.62	253.12
61.00	2393.28	181.17			61.00	3514.31	256.05
62.00	2429.69	181.33			62.00	3573.01	258.97
63.00	2465.97	181.49			63.00	3631.70	261.90
64.00	2502.14	181.66			64.00	3690.40	264.83
65.00	2538.18	181.82			65.00	3749.09	267.75
66.00	2574.11	181.98			66.00	3807.79	270.68
67.00	2609.93	182.14			67.00	3866.48	273.60
68.00	2645.63	182.31			68.00	3925.18	276.53
69.00	2681.22	182.47			69.00	3983.87	279.45
70.00	2716.70	182.63			70.00	4042.57	282.38
71.00	2752.08	182.79			71.00	4101.26	285.30
72.00	2787.36	182.96			72.00	4159.96	288.23
73.00	2822.53	183.12			73.00	4218.65	291.15
74.00	2857.60	183.28			74.00	4277.35	294.08
75.00	2892.58	183.44			75.00	4336.05	297.00
76.00	2927.46	183.61			76.00	4394.74	299.93
77.00	2962.25	183.77			77.00	4453.44	302.85
78.00	2996.94	183.93			78.00	4512.13	305.78
79.00	3031.55	184.10			79.00	4570.83	308.71
80.00	3066.08	184.26			80.00	4629.52	311.63
81.00	3100.51	184.42			81.00	4688.22	314.56
82.00	3134.87	184.58			82.00	4746.91	317.48
83.00	3169.15	184.75			83.00	4805.61	320.41
84.00	3203.35	184.91			84.00	4864.30	323.33
85.00	3237.48	185.07			85.00	4923.00	326.26
86.00	3271.53	185.23			86.00	4981.69	329.18
87.00	3305.51	185.40			87.00	5040.39	332.11
88.00	3339.42	185.56			88.00	5099.08	335.03
89.00	3373.27	186.06			89.00	5157.78	337.96
90.00	3407.05	187.89			90.00	5216.47	340.88
91.00	3440.77	189.72			91.00	5275.17	343.81

92.00	3474.43	191.55
93.00	3508.03	193.38
94.00	3541.57	195.22
95.00	3575.05	197.05
96.00	3608.48	198.88
97.00	3641.85	200.71
98.00	3675.17	202.54
99.00	3708.44	204.38
100.00	3741.66	206.21
101.00	3774.84	208.04
102.00	3807.97	209.87
103.00	3841.05	211.70
104.00	3874.09	213.54
105.00	3907.09	215.37
106.00	3940.04	217.20
107.00	3972.96	219.03
108.00	4005.84	220.86
109.00	4038.69	222.70
110.00	4071.50	224.53
111.00	4104.28	226.36
112.00	4137.03	228.19
113.00	4169.75	230.02
114.00	4202.44	231.86
115.00	4235.10	233.69
116.00	4267.74	235.52
117.00	4300.35	237.35
118.00	4332.94	239.18
119.00	4365.52	241.02
120.00	4398.07	242.85
121.00	4430.60	244.68
122.00	4463.12	246.51
123.00	4495.62	248.34
124.00	4528.12	250.17
125.00	4560.59	252.01
126.00	4593.06	253.84
127.00	4625.52	255.67
128.00	4657.98	257.50
129.00	4690.43	259.33
130.00	4722.87	261.17
131.00	4755.31	263.00
132.00	4787.75	264.83
133.00	4820.19	266.66
134.00	4852.63	266.58
135.00	4885.08	265.23
136.00	4917.52	263.88
137.00	4949.97	262.52
138.00	4982.43	261.17
139.00	5014.88	259.81
140.00	5047.34	258.46
141.00	5079.80	257.11
142.00	5112.26	255.75
143.00	5144.73	254.40
144.00	5177.20	253.05
145.00	5209.67	251.69
146.00	5242.14	250.34
147.00	5274.62	248.98
148.00	5307.10	247.63
149.00	5339.58	246.28
150.00	5372.07	244.92
151.00	5404.56	243.57
152.00	5437.05	242.22
153.00	5469.54	240.86
154.00	5502.04	239.51
155.00	5534.54	238.15
156.00	5567.04	236.80
157.00	5599.55	235.45
158.00	5632.06	234.09
159.00	5664.57	232.74
160.00	5697.09	231.39
161.00	5729.61	234.02
162.00	5762.13	237.66
163.00	5794.65	241.30
164.00	5827.18	244.93
165.00	5859.71	248.57
166.00	5892.24	252.20
167.00	5924.77	255.84
168.00	5957.31	259.48
169.00	5989.85	263.11
170.00	6022.39	266.75
171.00	6054.92	270.39
172.00	6087.47	274.02
173.00	6120.01	277.66
174.00	6152.55	281.29
175.00	6185.09	284.93
176.00	6217.64	288.57
177.00	6250.18	289.66

92.00	5333.86	346.74
93.00	5392.56	349.66
94.00	5451.25	352.59
95.00	5509.95	355.51
96.00	5568.64	358.44
97.00	5627.34	361.36
98.00	5686.03	364.29
99.00	5744.73	367.21
100.00	5803.42	370.14
101.00	5862.12	373.06
102.00	5920.81	375.99
103.00	5979.51	378.91
104.00	6038.20	381.84
105.00	6096.90	384.77
106.00	6155.59	387.69
107.00	6214.29	390.62
108.00	6272.98	393.54
109.00	6331.68	396.47
110.00	6390.37	399.39
111.00	6449.07	402.32
112.00	6507.76	405.24
113.00	6566.46	408.17
114.00	6625.15	411.09
115.00	6683.85	414.02
116.00	6742.54	416.94
117.00	6801.24	419.87
118.00	6859.93	422.79
119.00	6918.63	425.72
120.00	6977.32	426.47
121.00	7036.02	425.05
122.00	7094.71	423.62
123.00	7153.41	422.20
124.00	7212.10	420.77
125.00	7270.80	419.35
126.00	7329.50	417.92
127.00	7388.19	416.50
128.00	7446.89	415.07
129.00	7505.58	413.65
130.00	7564.28	412.22
131.00	7622.97	410.80
132.00	7681.67	416.55
133.00	7740.36	429.47
134.00	7799.06	442.39
135.00	7857.75	455.31
136.00	7916.45	468.23
137.00	7975.14	481.15
138.00	8033.84	494.07
139.00	8092.53	506.99
140.00	8151.23	519.91
141.00	8209.92	532.83
142.00	8268.62	545.75
143.00	8327.31	558.67
144.00	8386.01	559.52
145.00	8444.70	548.31
146.00	8503.40	537.09
147.00	8562.09	525.88
148.00	8620.79	514.66
149.00	8679.48	503.45
150.00	8738.18	492.23
151.00	8796.87	481.02
152.00	8855.57	469.80
153.00	8914.26	458.59
154.00	8972.96	447.37
155.00	9031.65	441.76

Appendix 3: Results for Lochnagar fossil samples: no. taxa per sample; N2; WA-PLS (2) diatom inferred pH reconstruction (estimated mean values and standard errors of prediction

Sample Level	No. Taxa	N2	Lower est. error	WA-PLS(2) inferrd pH	Upper est. error
0.0	25	23.87	5.57	5.93	6.28
0.2	28	26.37	5.45	5.80	5.93
0.4	26	23.86	5.36	5.73	5.93
0.6	24	22.29	5.34	5.70	5.93
1.0	28	25.71	5.41	5.76	5.93
1.2	22	20.11	5.39	5.74	5.93
1.4	22	20.85	5.47	5.82	5.93
1.6	26	23.64	5.47	5.82	5.93
1.8	23	20.90	5.23	5.59	5.93
2.0	27	24.75	5.54	5.89	5.93
2.2	27	24.62	5.51	5.86	5.93
3.0	22	20.85	5.18	5.54	5.93
4.0	26	24.88	5.29	5.66	5.93
5.0	29	27.55	5.14	5.51	5.93
6.0	26	24.92	5.02	5.41	5.93
7.0	29	26.74	5.22	5.61	5.93
8.0	22	20.92	5.03	5.39	5.93
9.0	37	35.74	5.47	5.83	5.93
10.0	35	32.98	5.51	5.86	5.93
11.0	33	31.36	5.63	6.03	5.93
12.0	39	37.34	5.71	6.13	5.93
13.0	34	32.54	5.26	5.64	5.93
14.0	39	37.39	5.52	5.88	5.93
15.0	35	33.72	5.58	5.94	5.93
16.0	30	28.56	5.62	5.98	5.93
17.0	34	32.62	5.67	6.02	5.93
18.0	35	33.63	5.62	5.99	5.93
19.0	39	37.62	5.75	6.14	5.93
20.0	30	28.29	5.47	5.84	5.93
20.2	41	39.18	5.55	5.94	5.93
21.2	40	38.06	5.72	6.12	5.93
22.0	35	33.82	5.91	6.31	5.93
23.0	39	37.65	5.93	6.33	5.93
24.0			5.86	6.23	5.93
25.0	40	38.75	5.86	6.28	5.93
26.0	35	33.94	5.61	5.96	5.93
27.0	36	34.30	5.58	5.95	5.93
28.0	35	33.83	5.82	6.26	5.93
29.0	36	34.54	5.56	5.93	5.93
30.0	31	29.99	5.84	6.20	5.93
31.0	41	39.56	5.67	6.03	5.93
32.0	41	39.51	5.45	5.81	5.93
33.0	40	38.49	5.98	6.37	5.93
34.0	36	34.87	5.94	6.30	5.93
35.4	30	28.95	6.01	6.45	5.93
36.8	35	34.04	5.82	6.25	5.93
37.8	40	38.61	6.12	6.52	5.93
38.8	38	36.30	5.59	5.95	5.93
39.6	39	37.80	5.62	5.99	5.93
40.0	28	26.43	5.60	5.96	5.93
41.2	37	35.85	6.05	6.41	5.93
42.0	37	35.43	5.87	6.22	5.93
44.0	29	27.50	6.13	6.57	5.93
44.8	40	38.10	5.94	6.30	5.93
46.0			5.98	6.34	5.93
47.6	41	38.99	5.72	6.09	5.93
48.6	39	37.15	5.76	6.13	5.93
49.4	39	36.70	5.51	5.88	5.93
50.0	31	29.58	6.01	6.43	5.93
50.6	37	35.57	5.82	6.18	5.93
51.6	32	30.69	5.75	6.11	5.93
53.0	27	25.74	5.83	6.22	5.93
53.8	34	32.31	5.63	5.98	5.93
54.8	37	35.50	5.62	5.99	5.93
55.0	37	35.12	5.70	6.08	5.93
56.0	41	39.42	5.76	6.12	5.93
57.2	43	41.28	5.78	6.13	5.93
58.6	38	36.29	5.69	6.06	5.93
60.0	34	32.64	6.08	6.47	5.93
60.8	37	35.08	5.66	6.02	5.93
62.0	37	35.20	5.69	6.06	5.93
63.6	38	36.45	5.60	5.96	5.93
65.0	41	38.70	5.76	6.12	5.93
66.0	34	32.75	5.77	6.15	5.93
66.8	42	40.35	5.78	6.15	5.93
67.6	34	32.64	5.79	6.15	5.93
69.2	35	33.09	5.67	6.05	5.93
69.8	32	30.38	6.02	6.38	5.93
70.0	32	30.33	6.02	6.47	5.93
71.0	33	31.42	5.72	6.09	5.93
71.8	38	36.08	5.96	6.33	5.93
72.8	30	28.60	5.73	6.12	5.93
74.2	32	30.48	5.70	6.09	5.93
75.0	34	32.85	5.69	6.05	5.93
76.4	34	32.42	5.50	5.88	5.93
77.6	34	32.22	5.82	6.23	5.93
78.8	41	38.88	5.87	6.29	5.93
79.8	44	42.01	5.74	6.11	5.93
80.0	32	30.73	5.94	6.30	5.93
81.2	31	29.80	5.88	6.25	5.93
83.4	44	41.76	5.86	6.22	5.93
84.8	36	34.37	5.80	6.16	5.93
86.4	35	33.68	5.93	6.29	5.93
87.8	38	36.62	5.79	6.16	5.93
89.2	41	39.56	5.87	6.24	5.93
90.0	33	31.43	5.91	6.27	5.93
90.8	43	41.11	5.71	6.10	5.93
91.0	37	35.73	5.80	6.19	5.93
91.2	38	35.94	5.70	6.10	5.93
91.4	32	30.38	5.54	5.96	5.93
93.2	38	36.80	5.58	5.96	5.93
95.4	35	32.32	5.52	5.96	5.93

96.4	36	34.36	5.96	6.32	5.93
97.8	42	40.17	5.50	5.88	5.93
98.8	38	36.54	5.68	6.05	5.93
99.8	27	26.03	5.78	6.19	5.93
100.0	38	35.86	6.12	6.48	5.93
101.0	38	36.12	6.08	6.44	5.93
102.0	37	35.25	5.96	6.32	5.93
103.0	35	32.94	5.82	6.19	5.93
104.0	35	33.62	5.96	6.33	5.93
105.0	36	34.48	5.89	6.25	5.93
106.0	36	34.61	5.73	6.09	5.93
107.0	27	25.91	5.99	6.36	5.93
108.0	33	31.60	6.07	6.46	5.93
109.0	37	35.66	5.97	6.42	5.93
110.0	31	29.54	6.15	6.51	5.93
111.0	33	31.76	5.96	6.32	5.93
112.0	31	29.50	5.95	6.35	5.93
114.0	36	34.14	5.78	6.16	5.93
115.0	37	35.26	5.95	6.35	5.93
116.0	25	23.91	6.00	6.43	5.93
117.0	36	34.44	6.17	6.58	5.93
118.0	26	25.22	5.93	6.29	5.93
119.0	27	25.44	6.19	6.54	5.93
120.0	38	36.55	5.62	5.98	5.93
121.0	32	30.57	6.00	6.36	5.93
122.0	34	32.96	5.79	6.18	5.93
123.0	36	34.84	5.87	6.23	5.93
124.0	37	35.79	6.13	6.53	5.93
125.0	35	33.66	6.01	6.42	5.93
126.0	34	32.61	5.91	6.27	5.93
127.0	37	35.33	6.16	6.57	5.93
128.0	33	31.67	6.12	6.53	5.93
130.0	34	32.49	5.99	6.39	5.93
131.0	33	31.41	6.00	6.36	5.93
132.0	39	37.16	5.90	6.26	5.93
133.0	36	34.05	5.85	6.20	5.93
134.0	34	32.41	5.77	6.15	5.93
135.0	39	37.75	5.76	6.13	5.93
137.0	33	32.11	5.73	6.13	5.93
138.0	38	36.44	5.74	6.10	5.93
139.0	38	36.50	5.81	6.17	5.93
140.0	34	32.33	6.06	6.41	5.93
141.0	31	29.67	6.03	6.41	5.93
142.0	33	31.42	6.06	6.51	5.93
143.0	34	32.54	5.93	6.29	5.93
144.0	34	32.54	6.05	6.42	5.93
145.0	39	37.16	6.18	6.58	5.93
146.0	38	36.44	6.09	6.49	5.93
147.0	35	33.36	6.06	6.47	5.93
147.8	35	33.77	5.79	6.18	5.93
148.6	30	28.74	5.83	6.20	5.93
149.4	34	32.79	5.92	6.28	5.93
150.0	27	25.71	6.37	6.85	5.93
150.4	34	32.93	6.17	6.60	5.93
151.4	35	33.57	6.09	6.53	5.93
152.4	40	38.17	5.80	6.17	5.93
153.2	34	32.85	6.00	6.43	5.93
154.2	32	31.04	5.85	6.21	5.93
155.6	33	31.94	5.85	6.21	5.93
156.6	35	33.80	5.74	6.10	5.93
157.6	30	28.54	6.07	6.43	5.93
160.0	36	34.58	5.83	6.26	5.93
160.6	35	33.95	5.58	5.94	5.93
161.4	36	34.57	5.81	6.18	5.93
162.2	28	26.86	5.77	6.13	5.93
163.2	32	30.65	5.69	6.08	5.93
164.2	29	28.05	6.00	6.40	5.93
165.2	39	37.31	5.72	6.09	5.93
166.2	32	30.57	5.64	6.00	5.93
167.2	31	29.42	5.55	5.95	5.93
168.2	34	32.32	5.72	6.09	5.93
168.8	36	34.48	5.71	6.07	5.93
169.6	30	29.13	5.97	6.35	5.93
170.0	30	28.66	5.84	6.24	5.93
170.4	33	31.59	6.03	6.40	5.93
171.2	37	35.48	5.93	6.29	5.93
172.4	33	31.53	5.87	6.27	5.93
173.2	42	40.44	5.87	6.24	5.93
174.6	40	37.87	5.91	6.29	5.93
175.4	39	36.93	5.98	6.35	5.93
176.2	43	41.66	5.82	6.19	5.93
177.8	36	34.24	5.75	6.11	5.93