Peatlands, volcanoes and climate: Ecological and palaeoecological studies in Alaska and Scotland
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Peatlands, volcanoes and climate: ecological and palaeoecological studies in Alaska and Scotland

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ABSTRACT

This thesis investigates direct and indirect volcanic impacts on peatlands using palaeoecological and ecological techniques. The primary approach used is palaeoecological studies across tephra layers. A multi-proxy methodology was adopted including testate amoebae, humification and outline macrofossil analysis supported by radiocarbon dating. To allow quantitative interpretation of testate amoebae results a transfer function model was developed for surface wetness and pH. To examine whether it is justified to use tephra layers as evidence of volcanic activity an experiment was carried out to investigate tephra taphonomy. Results show that tephra does move through peat but the majority remains at the surface. In an attempt to characterise the palaeoecological response to volcanic acid deposition an experiment was conducted applying tephra and acids to a Scottish peatland. Results show drastic impacts on peatland plants but impacts on other variables were more equivocal.

For the palaeoecological studies a series of peatland sites were sampled in southeast Alaska and on the Kenai Peninsula in south-central Alaska. A number of microscopic and visible tephras were located and subjected to electron microprobe analysis to aid their identification. Results show the great potential of micro-tephrochronology to extend the distribution of tephra layers in Alaska. Furthermore, results highlight the great size of several eruptions, improve the dating of others and show the presence of previously unrecognised tephras. The macrofossil and testate amoebae results show impacts associated with some tephras but not all. The humification results are considered unreliable due to a methodological problem. The most likely cause of the impacts is through volcanic acids and gases or other chemicals adhering to tephra shards. The variability of impacts may be due to the season of eruption. These results have implications for the volcano-climate system, peatland conservation and agriculture.
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- The testate amoebae transfer function study was carried out collaboratively with Keiko Kishaba and Edward Mitchell, University of Alaska Anchorage. Testate amoebae counting from two sites and the species-environment correlations are their work. Edward Mitchell’s contribution in this study and with testate amoebae identification is much appreciated.

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CHAPTER 1. INTRODUCTION & LITERATURE REVIEW

Peatlands are organic wetlands characterized by an actively growing plant layer and thick accumulations of partially decomposed plant detritus. They cover perhaps 400 million ha of the earth’s surface and are particularly abundant across the northern latitudes of Eurasia and North America (Charman 2002). Peatlands fill important roles in the global carbon and hydrological cycles, constitute large resources of biodiversity, provide economic functions and can be used to investigate human and environmental history.

Throughout the world, layers of volcanic ash (tephra) are found preserved in peat. This suggests the question: ‘what impacts do volcanic eruptions have on peatlands?’ This is an issue that has not been widely addressed; the answer may have important implications for the functions provided by peatlands, which may in turn have wider environmental implications. This thesis investigates volcanic impacts on peatlands using palaeoecological and neoeccological approaches.

1.1 VOLCANIC IMPACTS ON VEGETATION
1.1.1 Proximal volcanic impacts

Volcanoes affect vegetation in several ways. Immediately adjacent to a volcanic source, lava flows, pyroclastic flows and lahars will almost certainly kill all plant life through a combination of extreme heat, manual breakage and the depth of the resulting deposit (Griggs 1918, 1922, Vucetich & Pullar 1963, Winner & Casadevell 1983). In explosive eruptions plant life may also be killed by the sheer heat and violent winds of a volcanic blast (Griggs 1919, Eggler 1948). The sterile volcanic substrates left by these events form the basis for a primary succession sequence. Several studies have investigated revegetation of volcanic landscapes in various regions of the world (Eggler 1941, Fridriksson 1975, 1987, Whittaker et al. 1989, 1992, Grishin et al. 1995, Del Moral 1998, Dale & Adams 2003).

Various factors affect plant re-colonization, perhaps the most important of these is the isolation of the deposit (Fridriksson 1975, 1987, Del Moral 1998). The rate of initial
colonization and the species initially colonizing a deposit will depend on proximity to, and the community composition of surrounding unaffected areas. Lava flows follow the topography of the landscape this can often leave small unaffected refugia within which plants can survive to colonize the lava surface with relative rapidity (Kent et al. 2001). The specific pattern of plant recolonization may depend on a complex variety of environmental factors (surface moisture, temperatures, exposure) as well as variability in volcanic substrate (surface texture, chemical composition) and stochastic chance (Fridriksson 1987, Whittaker et al. 1989, Wood & Del Moral 1989, Bjarnason 1991, Del Moral 1998). The timing and direction of succession can be heavily affected simply by the chance event of when the seeds of a species arrive on the surface (Fridriksson 1975, 1987, Whittaker et al. 1992). In unfavourable conditions plant colonization can take an extremely long time, large areas of pyroclastic deposits from the 1912 eruption of Katmai (southwest Alaska) are still largely uncolonized due to the harsh physical environment of the surface. Interestingly, Vucetich & Pullar (1963) suggested that the deposition of thick tephra layers may have speeded the post-glacial return of vegetation to New Zealand’s North Island by providing a rooting medium.

Initial colonizing plants are often r-selected ‘weedy’ species, generally with wind-dispersed seeds and adapted to the low nutrient content of volcanic substrates (Wilmshurst & McGlone 1996, Wood & Del Moral 1998). Griggs (1922) noted the rapid establishment and spread of such a species, the horsetail Equisetum arvense on Katmai deposits, this species was also the first to establish on deposits from the 1980 eruption of Mt. St. Helens. The establishment of species with animal dispersed seeds will depend on the presence of suitable vector species, which is likely to be limited in the early stages of succession (Fridriksson 1975, 1987, Wood & Del Moral 1988, Whittaker et al. 1989). The plant community of recently colonized volcanic substrates will usually have a very low diversity (Fridriksson 1987, Burnham 1994). Community development will proceed as species and biomass accrue on the deposit eventually reaching a climax community (Del Moral 1998). Recolonization may be disrupted or re-directed by subsequent human, geomorphological, volcanic and seismic activity (Whittaker et al. 1989, Dale & Adams 2003).
Beyond the zone of direct vegetation burial, plants may be indirectly affected by volcanic action. Lava, pyroclastic flows, tephra fall and lightning may ignite fires potentially destroying vegetation across a wide area initiating a secondary succession on the burned landscape. Extreme ‘volcano weather’ including strong winds and extreme precipitation may also have an impact on vegetation. Vucetich & Pullar (1963) note the death of vegetation through the formation of temporary lakes due to the damming of rivers by volcanic products.

1.1.2 Distal volcanic impacts

Following eruptions, volcanic ash (tephra) may be deposited across a large area burying plants. This poses several stresses on plants. Tephra on leaves will block light inhibiting photosynthesis (Cook et al. 1980, Clarkson & Clarkson 1994). Tephra is composed of sharp, angular glass particles making it highly abrasive to plant surfaces (Bjarnason 1991). Griggs (1922) noted destruction of plant leaves by windblown tephra following the Katmai 1912 eruption. Tephra on plant leaves may also potentially block stomata and therefore gas exchange (Eggler 1948), mechanisms analogous to the impact of particulate air pollutants (Beckett et al. 1998). Tephra on the ground may limit gas exchange between the soil and the atmosphere, potentially effecting supply of Oxygen to plant roots (Eggler 1948). Tephra on plant surfaces can result in reflectance of solar radiation producing a relative cooling of the leaves (Cook et al. 1980). Finally, the sheer weight of tephra, particularly when wet may damage plants by crushing tissues, stripping leaves and breaking limbs (Eggler 1948, Wilcox 1959, Cook et al. 1980).

The ability of plants to survive these stresses from tephra burial depends on a number of factors. Simplest of these is the size of the plant, it is well established that taller plants may survive tephra burial while smaller plants do not (Eggler 1948, Antos & Zobel 1985a). Under moderate tephra fall the leaves of larger plants such as trees may be largely tephra-free while smaller understorey plants are totally buried. Tephra fall on forests may often kill the understorey while trees survive (Zobel & Antos 1997). The depth of tephra burial required to destroy forests seems to be variable between studies from around 40cm to perhaps several meters (Eggler 1948, Griggs 1919, Vucetich &
Pullar 1963). By contrast a few centimeters of tephra may be sufficient to kill bryophytes (Zobel & Antos 1997).

The key method by which plants adapt to tephra burial is by producing new adventitious roots, rhizomes and vertical shoots to penetrate the tephra layer (Antos & Zobel 1985a & b). This can lead to plants gaining a distinctive ‘two-tier’ root system (Griggs 1919, Antos & Zobel 1985). The phenotypic plasticity to enable plants to adapt in this way may be the key determinant of survival. Griggs (1919) described the presence of poplar and willow in Katmai tephra deposits, the willows had produced adventitious roots and were thriving while the poplar had not produced new roots and were severely effected. New growth through shoots produced by buried plants may be impaired if the tephra develops a more solid crust which cannot be penetrated (Zobel & Antos 1997). Some plant species may survive tephra burial by entering a state of dormancy and regrowing when tephra is removed. Zobel & Antos (1997) exhumed plants eight years after the eruption and showed new growth of several species. Griggs (1919) described new plant growth along erosion cracks in the tephra layer. It is clear that some plant species are better adapted to survive repeated burial by tephra than others. Repeated eruptions may exclude sensitive species from volcanically active regions (Zobel & Antos 1997). Tephra deposition may ultimately improve the physical and chemical quality of soils, resulting in more productive vegetation growth (Vucetich & Pullar 1963, Cronin & Hedley 1997).

An important factor in determining plant survival may be the season of eruption. Generally eruptions during winter when plants are dormant are likely to have more limited effects than eruptions during the growing season. For the 1980 Mt St Helens eruption Zobel & Antos (1997) describe the case of Veratum viride (Hellebore), at lower altitudes the plant had started to produce shoots, these individuals were not able to cope with tephra burial. At higher altitudes plants were dormant at the time of the eruption and were subsequently able to produce shoots to penetrate the tephra. Snow cover may protect buried plants from the worst of tephra impacts, this can potentially result in an inverse size effect with trees killed while shrubs buried under snow are protected (Yamaguchi et al. 1993). Plant survival can depend on the precise location of a plant with individuals sheltered by microtopography or even by a tree canopy more likely to
survive (Griggs 1919). Indirect impacts on plants are also possible through volcanic impacts on predators (Wilcox 1959, Cook et al. 1980). Plant stress due to tephra impacts may increase vulnerability to disease (Cook et al. 1980).

Along with pyroclastic products, volcanoes also emit a large volume of gases to the atmosphere. The composition of these gases is variable but is generally dominated by CO₂, SO₂, HCl and HF (Wilcox 1959, Le Guern et al. 1988, Symonds et al. 1988, Delmelle et al. 2002). In explosive eruptions these gases will largely be injected into the stratosphere, however in less explosive effusive eruptions the majority of gases may remain in the troposphere (Le Guern et al. 1988). Volcanic compounds may be deposited as a gas, as dry deposition, acidic precipitation, acidic aerosols and adhering to tephra particles (Rose 1977, Oskarsson 1980, Delmelle et al. 2001). In the atmosphere SO₂ may combine with water to form a sulphuric acid aerosol, acidic precipitation has been noted following several eruptions (Griggs 1922, Delmelle et al. 2001, Le Guern et al. 1988). Following the 1912 Katmai eruption acidic rains were recorded 500Km away at Prince William Sound and chemically analyzed to show the presence of sulphuric acid. Anecdotal accounts are documented over 2000Km away in Vancouver, British Columbia where rain was reportedly sufficiently acidic to bleach clothing (Griggs 1919, 1922). The extent of acidic deposition will depend on a number of factors including eruption size and chemical composition, extent of tephra scavenging, wind speed and direction, landscape topography and rainfall patterns (Clarkson & Clarkson 1994, Aiuppa et al. 2001, Armienta et al. 2002, Delmelle et al. 2002).

Volcanic gases and precipitation have been observed to effect plant growth in various ways. Leaves have shown lesions, burnt spots and die back from the edges. Similar effects have also been observed on fruit. In more extreme situations total defoliation and plant death have been noted (Parnell & Burke 1990, Clarkson & Clarkson 1994, Delmelle et al. 2002). These effects are analogous to those produced in experimental studies of SO₂ exposure (Caput et al. 1978). Such impacts may have been mistaken for heat damage in some studies (Wilcox 1959) and may be longer lasting than the physical impact of tephra on plants (Whittaker et al. 1992). Species differ in their ability to survive such exposure with characteristics such as thick waxy leaves making some species more resistant than others; such resistant species may expand their
distribution. Delmelle et al. (2001) noted the loss of tree species from heavily affected areas. Vegetation may be further affected through volcanic soil acidification (Delmelle et al. 2001, 2002). Studies of non-volcanic acidification suggest acidity can affect plant growth by interference with ion-transport and increases in metal bioavailability as well as direct H+ ion toxicity. Plants may respond by reducing root growth (Marschner 1995).

The most convincing evidence for the distal impacts of volcanic acidity comes from the historical record. Particularly convincing evidence is provided by descriptions of the impact of the Laki (Iceland) eruption of 1783-4 and coincident eruptions of Italian volcanoes (Thorarinsson 1981, Sigurdsson 1982, Camuffo & Enzi 1995, Grattan & Charman 1994, Grattan & Gilbertson 1994, Grattan & Pyatt 1994, Grattan et al. 1998). Numerous accounts describe impacts on crops including discoloration, loss of fruits, formation of lesions, defoliation and charring. Many of these accounts equate this damage with that caused by frost or drought. The British chronicler Gilbert White writes that 'blades of wheat in several fields are turned yellow and look as if scorched by frost' (White in Grattan et al. 1998). In Holland S.P. Van Swinden (2001 discussed by Thordarson & Self 2001) wrote that 'the leaves of many trees were faded, grass and vegetables appeared likewise. Leaves and fruits fell as if in autumn: afterwards the whole country looked desolate'. Another British account notes that 'the aristae of the barley which was coming into ear became brown and weathered at their extremities, as did the leaves of oats: the rye had the appearance of being mildewed; so that the farmers were alarmed for those crops' (Cullum in Grattan & Pyatt 1994). In Denmark, Holm (1784, cited in Thorarinson 1981) wrote that 'because of this rain, leaves on the trees were partly burnt through and the grass on the ground turned almost black'. The effects described are often highly species specific, one account describes impacts on several species (including cherry, peach and hazel trees) but not on others (mulberry, fig and vines; Cullum in Grattan & Pyatt 1994). Other accounts describe impacts on several grain species but not on wheat. The symptoms described are consistent with those of volcanic gases, aerosols and acid rain. While there may be various modes of impact, the bulk of the symptoms are consistent with damage by sulphur dioxide or sulphuric acids (Grattan & Pyatt 1998). Camuffo & Enzi (1995) suggest that calcium fluorsilicate adhering to tephra (derived from volcanic HF) could have caused the burning effects on leaves. These
authors also suggest that volcanic aerosols may have removed plant cuticles, increasing vulnerability to environmental stress, parasites and disease. Camuffo & Enzi (1995) suggest that impacts through volcanic aerosols have been relatively common in Italy over the last five hundred years. These historical records suggest that the event in 1783 had impacts across much of western Europe, with accounts from Scotland, England, Holland, Denmark, Germany, Switzerland and Italy.

Plants can be heavily affected by both the proximal and distal impacts of volcanic activity. Close to the source plants will be directly affected by volcanic activity including volcanic blasts, lava and pyroclastic flows. At greater distance the most significant impacts may be produced through tephra burial. The impacts of volcanic acids may extend the furthest from the volcano, potentially producing affects at distances over 1000Km. Different plants and ecosystems may be differently sensitive to volcanic products, factors such as growth form and phenotypic plasticity may be important in determining survival.
1.2 VOLCANIC IMPACTS ON PEATLANDS

1.2.1 Ecological studies

Many volcanic eruptions occur in regions with abundant peatlands, however neoecological studies have not widely addressed the issue of volcanic impacts on these ecosystems. Griggs (1919) noted the recovery of vegetation on an ‘upland bog’ buried by tephra from Katmai (1912) including the return of several species (*Athyrium cyclosorum, Trientalis arctica, Ledum decumbens, Betula rotundifolia, Empetrum nigrum, Vaccinium uliginosum, Cornus suecica and Vitis-idaea vitis-idaea*). It is perhaps notable that this list does not include any *Sphagnum* species, which would presumably have been present on an upland bog in southwest Alaska. Rigg (1914) noted that many bogs of the region were totally buried by this tephra. The presence of tephra layers in peat in Alaska and other volcanic regions of the world suggest that volcanic impacts on peatlands may occur with relative regularity (Dachnowski-Stokes 1941).

In an experimental approach, Hotes et al. (2004) added layers of tephra and ground glass simulating tephra to plots on a mire in Hokkaido, Japan. Tephra was applied in various quantities up to a layer 6cm thick, of various grain size and at two different times of year. Results showed substantial changes in pore water chemistry. Particularly notable were increases in pH, electrical conductivity, SiO₂, SO₄²⁻ and Na⁺. Several changes in species composition were noticed with some species being lost although many of these later became re-established. *Sphagnum* species were particularly affected, especially at higher applications with vascular plants increasing in relative abundance. The scale of the impacts was related to the size of the layer with greater impacts under larger layers and fine-grained tephras had greater impacts than coarse-grained. Impacts were highly seasonal with tephra applications in early growing season being most effective. This study provides a valuable contribution to the subject but is limited in some respects. Perhaps most serious is the composition of the applied ‘tephra’ including the use of non-volcanic glass. This glass cannot be assumed to have the same composition as real tephra and therefore the apparent changes to pore-water chemistry and consequent vegetation changes may well not be representative of real eruptions. In addition the genuine tephra applied in some plots was from old buried deposits, it is therefore likely to
have been subject to previous leaching. There was no simulation of the effects of chemicals adhering to the tephra. Overall a very limited amount of ecological work has been devoted to volcanic impacts on peatlands and a great many issues remain unclear.

1.2.2 Palaeoecological studies

One method of investigating volcanic impacts on peatlands is through the palaeoecological record. Crowley et al. (1994) looked at the effects of thick (<40cm) tephra layers on a peatland environment, inferred from Cretaceous coal beds in Utah, USA. Their results suggested several possible impacts on the mire. The pH of the mire pore waters may have increased following tephra deposition leading to an increase in microbial activity. Alternatively chemicals contained within the ash may have led to charring of the mire vegetation. Tephra may also have created a semi-impermeable layer causing surface ponding of water and allowing the expansion of Sphagnaceae species (Crowley et al. 1994). In another geological study Kovar-Eder et al. (2001) investigated the stratigraphy of an Austrian lignite deposit representing a Miocene backswamp environment. Results demonstrated that lapilli deposition caused widespread stripping of plant leaves and buds, which became preserved in the sediments.

Giles et al. (1999; also see Giles 1999) investigated pollen changes across the Holocene Kaharoa tephra (2-3cm thick) in a New Zealand peatland. Results showed significant disturbance including increases in degraded pollen and a particularly notable increase in Leptospermum pollen. They suggested that impacts may have occurred through the impact of volcanic acids or the physical impact of tephra on plants possibly combined with hydrological changes.

In Japan, Hotes et al. (2001) investigated the stratigraphy of a soligeneous mire containing numerous tephra layers as well as other mineral layers. Their results showed limited evidence for any impact; although some layers were associated with changes in the macrofossil community, many more were not. In North America, Mehringer et al. (1977) encountered layers of Mazama and Glacier Peak tephra in a peat-stratigraphic sequence from Montana. Pollen analysis showed no convincing evidence for impacts on vegetation. In Columbia, Kuhry (1988) investigated the pollen, spore and macrofossil
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stratigraphy of a topogenous mire exposed to repeated proximal volcanic influence. Mire development was initiated by volcanic activity due to obstruction of drainage by a lava flow; subsequent volcanic activity also lead to inundation episodes on the mire. More recent tephra falls have produced some detectable impacts on vegetation. This limited palaeoecological evidence shows a varying pattern, although it appears that volcanoes can produce impacts on peatlands this is not found in all studies.

Volcanic impacts on peatlands in Britain and Ireland

The possibility that past volcanism has affected peatlands in the British Isles was first suggested by Baillie & Munro (1988). This study noted clusters of extremely narrow tree-rings from Irish bog oaks, which the authors interpreted to represent a volcanically induced climatic deterioration caused by the cataclysmic eruption of Santorini (Thera). More recently, microscopic tephra layers have been found in numerous peatland sites in northern Britain and Ireland (Dugmore 1989, Pilcher & Hall 1992, Dugmore et al. 1995). Examining the palaeoecological record across these tephras allows the potential to investigate the impacts of these eruptions on the environment; in northern Scotland this was first attempted by Blackford et al. (1992). Results showed coincidence between the c.4000BP eruption of Hekla (Hekla-4) and a decline in Pinus pollen. At one site there was also a temporary peak in Sphagnum and in the other an apparent increase in Cyperaceae. The authors suggested two alternative hypotheses for this apparent impact: either a volcanic induced climatic deterioration or an impact through volcanic gases or precipitation.

This apparent linkage has not been noted in other studies. Hall et al. (1994) investigated pollen across a tephra later shown to be Hekla-4 in a northern Irish peatland. Contrary to the Scottish study they found no temporal link between the tephra layer and the decline of Pinus pollen. They suggested this as evidence that the events are unrelated, although Edwards et al. (1996) have noted that pine may not have been present on the site at this time, potentially undermining this conclusion (see also reply by Hall et al. 1996). Charman et al. (1995) examined pollen changes across three Holocene tephras in a northern Scottish peatland near to the sites used by Blackford et al. (1992). Results
showed variable impacts, across one tephra there is a marked change with loss of *Corylus/Myrica* and an increase of *Cyperaceae*, across another tephra there is little change and across a third (which may be Hekla-4) there is a significant increase in *Pinus*. This is curious as it would appear to show the opposite effect to that reported by Blackford *et al.* (1992). Some basic chemical analyses of the peat were also undertaken, interestingly results showed a peak of sulphur coincident with one of the tephra layers. On Shetland, Bennett *et al.* (1992) failed to determine a significant effect of tephra falls on vegetation. On Orkney, Edwards *et al.* (1994) showed that a minor peak in *Calluna* pollen and a trough in *Gramineae* coincide with a tephra peak of unknown source although the overall changes are minor.

In a more recent Irish study Caseldine *et al.* (1998) investigated pollen and humification changes across a tephra believed to be Hekla-4. Uniquely, this study investigated several profiles across the same tephra to investigate any spatial variation in the tephra-pollen relationship. Results showed an apparent wet-shift in one profile but this was not found in a further two locations. This illustrates potential inconsistency in response within sites and stresses the need for replicate data. Interestingly, accumulation rate changes appear to occur close to the tephra layer in all profiles. Hall (2003) investigated the impact of the mid-Holocene Lairg tephras in two raised bogs in Northern Ireland. There are few changes associated with tephra layers and none that are consistent between sites or tephras. Dwyer & Mitchell (1997) investigated the palaeoecological record across twin mid-Holocene tephra layers in a blanket mire from western Ireland. This study is particularly interesting as it also included non-pollen palynomorphs (spores and those testate amoebae which survive pollen preparation) and employed rate of change analysis to quantitatively investigate volcanic impacts. Results showed that the pine decline occurred prior to the tephra layers and there was little evidence for impacts upon regional pollen taxa. However there were several changes in pollen from mire species and the other palynomorphs coincident with the tephra layers. These include increases in *Cyperaceae, Narthecium ossifragum, Sphagnum* and an extremely prominent peak of the testate amoeba *Amphitrema flavum*. These changes are interpreted as a shift to wetter conditions and may indicate that the eruptions had impacts on the mire system without affecting regional vegetation.
Overall this research presents a confused picture with some studies suggesting reasonable evidence for volcanic impacts and other studies showing no such effects. If there was an impact, the acidification/tephra impact hypothesis would seem to be more reasonable than that of a volcanic induced climatic deterioration. It seems unlikely that these Icelandic eruptions are of sufficient magnitude to produce the severe and long-lasting climatic deterioration that would be required to produce the impacts suggested (Birks 1994, Grattan et al. 1999). On the narrow point of the correlation between Hekla-4 and the Pinus decline, the difference in results between the initial study of Blackford et al. (1992) and the subsequent studies could conceivably represent real ecological differences. The volume of Hekla-4 tephra deposited in northeast Scotland may be up to 700 times greater than that reported from Northern Ireland. It is therefore entirely possible that the scale of impacts in Scotland was much greater than those in Ireland with volcanic induced stress triggering a pine decline in Scotland but not Ireland. The lack of such a result in the Scottish study of Charman et al. (1995) is harder to explain but the lack of geochemical data means that we cannot be sure that Hekla-4 is one of the identified tephras.

To some extent the data are insufficient to answer the question of volcanic impacts in northern Britain and Ireland. Many of the studies have not used microprobe analysis to determine the provenance of the tephras, the resolution of some studies is low and most studies have been restricted to pollen analysis. A further complicating factor is that the widely studied Hekla-4 eruption coincides with a period of pre-existing climatic and environmental change; distinguishing a volcanic impact is therefore complicated. Although the majority of studies have failed to find convincing evidence of impacts the initial work of Blackford et al. (1992) has not been adequately repeated in Scotland. Therefore the question must remain open pending further research. Research using other proxy-records and on a greater number of tephras at other sites would also be productive.
1.2.3 The possible impact of volcanoes on peatlands - deduction and theory

There is relatively little direct research regarding the impact of volcanoes on peatlands. However, it is possible to make some assumptions about the possible modes of impact given the available research and research into the effects of anthropogenic pollutants.

Physical impacts on peatlands

As with plants in other ecosystems, peatland plants may be affected by tephra burial. Plants may be stressed by the inhibition of photosynthesis, abrasion, blocking of stomata and the sheer weight of tephra burial. As most peatland plants are relatively low growing depths of tephra burial that would not affect larger plants may kill them. Peatland bryophytes may be particularly vulnerable to the physical impact of tephra due to the low growth form and lack of a protective cuticle. Tephra burial may potentially affect peatland hydrology. Tephra layers could inhibit water penetration leading to surface ponding (Crowley et al. 1994). Alternatively, tephra could lead to improved aeration of the upper layers of peat (Hotes et al. 2004). If plants are widely killed this could lead to a reduction in evapo-transpiration and an increase in surface wetness.

Acidity impacts on peatland ecosystems

A further possible mechanism by which volcanoes may affect peatlands is through the impacts of volcanic acid rain. Although no studies have directly investigated the impact of volcanic acidity on peatlands, many studies have investigated the impact of anthropogenic acid deposition on various ecosystems including peatlands (Vangenechoten 1980, Gorham 1998). Peatlands are naturally acidic systems; however this does not mean they are unaffected by acidification. Probably the major means by which peatlands gain and maintain their low pH is through the high cation exchange capacity of Sphagnum, and to a lesser extent other plant species (Charman 2002). Sphagnum contains large amounts of polyuronic acids (around 30% by dry weight: Clymo 1987), which release H⁺ ions into bog waters in exchange for metal cations, reducing pH. Further acidity may be
contributed by the complex organic (humic and fulvic) acids produced by decomposition processes, although the extent to which this is an independent pathway is debatable (Hemond 1980, Gorham et al. 1984, Clymo 1987). Peatlands undergo natural acidification as they develop from fens (pH around 6) to bogs (pH around 4). As peatlands reach ombrotrophy there is no hydrological input of cations or removal of organic acids leading to an acidification trend (Gorham et al. 1984), which can be reconstructed by palaeoecology (Gorham et al. 1987a).

Ombrotrophic mires receive inputs from the atmosphere alone, as such they may be highly sensitive to air pollution (Proctor & Maltby 1998). Peatlands have little capacity for buffering inputs of acidity. The peat exchange complex is already strongly saturated by hydrogen ions so that deposited hydrogen ions are unlikely to be exchanged for metal cations and will lead to a pH drop (Gorham et al. 1984). Studies have shown a significant correlation between mean rainwater pH and surface water pH across the gradient of acid deposition in the UK (Proctor & Maltby 1998, Skiba et al. 1989). This illustrates the potential for anthropogenic acid rain to acidify peatlands and has also been demonstrated using experimental approaches (Sanger et al. 1994, Smith et al. 1993). The most sensitive sites are likely to be fens with waters low in bicarbonate alkalinity, in these sites anthropogenic acid rain could favour Sphagnum species and ultimately hasten the transition to ombrotrophy (Bayley et al. 1987, Gorham et al. 1987b). The extent of peatland acidification may be affected by the retention of deposited sulphur in a reduced form in the peat (Bayley et al. 1987). In times of drought this sulphur may be oxidized leading to the production of a sulphuric acid pulse with potentially significant ecological consequences (Gorham et al. 1987b, Proctor & Maltby 1998).

Acidification may affect peatland functioning by a variety of mechanisms. A feature of the natural acidification of peatlands is the reduced availability of nutrients. In acidified bogs, most nutrient cations (Ca, Mg, K etc) will be in the adsorbed state and largely unavailable to plants due to the abundance of H+ ions. Addition of strong mineral acids may worsen this oligotrophy (Gorham et al. 1984). Sanger et al. (1994) demonstrated lower base saturation in peats exposed to more acidic precipitation, this is likely to be due to leaching of base cations in acidified peats (Sanger et al. 1996). Furthermore, absorption of P is pH dependent and may be particularly affected by
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Acidification (Gorham et al. 1984). In other ecosystems many ecological affects are caused by the mobilization of toxic metals (Al in particular). The extent to which this may take place in peatlands is largely unknown (Gorham et al. 1984). Lee et al. (1987) note that Al ions are readily detectable in drainage waters from the highly acidified Southern Pennine peatlands. Acidification may also affect the activity of microorganisms and the processes they mediate such as nitrogen cycling and decomposition processes (Gorham et al. 1984, Sanger et al. 1996), affects on enzyme activity have also been shown (Press et al. 1985). Sanger et al. (1994) experimentally demonstrated reduced decomposition rates of Calluna vulgaris and Eriophorum angustifolium leaves exposed to acidic precipitation, this is believed to be due to reduced activity of enchytraeid worms. This study also demonstrated increased dissolved organic carbon (DOC) fluxes in drainage waters from more acidic peats.

Peatland plants will be directly or indirectly affected by acidification (Smith et al. 1993). This is well illustrated by the heavily acidified peatlands of the South Pennines. Since the industrial revolution numerous bryophytes have been lost and the mires have become sedge dominated (Gorham et al. 1984, 1987a, Lee et al. 1987). Sphagnum species have been particularly affected by this acidification, they are now virtually absent from areas in which palaeoecological studies show they were once widespread (Ferguson et al. 1978, 1980). The sensitivity of Sphagnum to sulphur pollutants has been shown by laboratory and field experiments (Ferguson et al. 1978, 1980). Sphagnum plants exposed to SO₂ gas or sulphuric acid show reduced growth rates, bleaching and ultimately death. Resistance varies between species, the minerotrophic S. recurvum is relatively resistant while S. tenellum and S. imbricatum are particularly sensitive (Ferguson et al. 1978). In general bryophyte species seem to be the most sensitive to acidification as the absence of a cuticle means they have little protection from a harsh physical environment (Gorham et al. 1987b). Conversely, long root systems anchored in the catotelm may help vascular plants to survive short-term pollution episodes (Ferguson et al. 1980). Loss of bryophyte and lichen diversity can provide evidence of the early effects of acidification on peatlands (Gorham et al. 1984, Skiba et al. 1989). In the field Hogg et al. (1995) investigated vegetation changes in a small mire exposed to acid deposition over an 11-year period. Over the period pH decreased by up to 1 unit while acid-sensitive species such as
Sphagnum squarrosum declined and more tolerant species such as Molinia caerulea expanded their coverage. Recent studies have attempted to apply critical loads as criteria for peatland acidification (Smith et al. 1993, Hormung et al. 1995, Wilson et al. 1995, Calver et al. 2004). Overall, it is clear that the impacts of acidification on peatlands are complex and not well understood. Potential impacts occur on many biological, chemical and physical processes and the complex interactions between them make reactions difficult to predict.

The impact of volcanic gas and acids on peatlands

The studies of anthropogenic acid rain strongly suggest the potential of volcanic acids to impact on peatlands. However this research cannot be directly applied to volcanic impacts as these studies consider longer-term acidification of a different composition. Volcanic acid rain is likely to contain less nitrate ions and greater amounts of Cl\(^-\) and F\(^-\) ions than anthropogenic acid precipitation. A volcanic acid precipitation event is likely to be more concentrated but shorter lived than anthropogenic acid deposition. The most likely volcanic impacts are through the direct impacts on peatland plants. Studies in other environments show the potential of volcanic gases and acid rain to cause damage to plant surfaces, defoliation and even death. It is likely that peatland plants could be similarly affected. The impact is likely to be species dependent, modern pollution studies show that bryophytes are often particularly vulnerable. It is uncertain whether a single pulse of acid rain would be sufficient to cause a significant change in peatland pH. This is likely to depend on the composition of the acid precipitation and the hydrological state of the peatland. If pH does substantially change then changes to the animal and microorganism community may occur. As with anthropogenic acid rain, the most vulnerable peatlands may be nutrient poor fens.

Volcanic impacts on methane flux- a feedback to the volcano-climate system?

One of the main carbon fluxes from peatlands is through methane. In the process of decomposition complex plant polymers are initially broken down to monomers
(sugars, amino acids etc) and subsequently to simpler compounds such as acetate and H₂ by fermenting bacteria (Schimel 2004). Methanogenic archaea derive energy and produce methane from these substrates by either fermenting acetate to produce methane and CO₂ or by oxidizing H₂ to H₂O using CO₂ which is reduced to CH₄ (Gauci et al. 2004).

An alternative pathway for metabolizing these substrates uses sulphate as an electron acceptor in anaerobic respiration, producing H₂S as a final product. This sulphate reducing pathway is more energy efficient than methanogenesis, therefore where sulphate is present, sulphate reducing bacteria are at a competitive advantage (Gauci et al. 2002). In wetlands with substantial SO₄²⁻ sources such as coastal salt marshes methane production is limited. However, in natural freshwater wetlands such as peatlands there is little external supply of electron acceptors and methane emission is significant. Methane is 21 times more climatically effective than CO₂ on a molecule for molecule basis (Gauci et al. 2002) and accounts for over 20% of the contemporary greenhouse warming trend (Schimel 2004). Northern peatlands account for around 30% of the total wetland methane flux (Nedwell & Watson 1995).

This methane flux may be affected by anthropogenic sulphate emissions. Several studies have used experimental manipulations to investigate the potential impact of sulphate deposition on methane flux. Initial studies used large infrequent applications (Fowler et al. 1995, Nedwell & Watson 1995, Watson & Nedwell 1998), more recent studies have used frequent smaller applications more typical of real sulphate deposition (Dise & Verry 2001, Gauci et al. 2002). Results demonstrate that only a low threshold of sulphate deposition is required to suppress methane flux. At high applications methane flux may be reduced by up to 45% (Schimel 2004). This methane suppression is highly temperature dependent, the greatest suppression occurs in cooler conditions (winter) when the methane flux is naturally lower (Gauci et al. 2002). This suppression of methane flux has globally significant implications. The modelling study of Gauci et al. (2004) estimates that this effect may currently reduce global methane emission by around 8% and up to 15% by 2030 (although this study assumes all wetlands react the same as peatlands and have no natural sulphate sources).

As has been previously discussed, volcanic eruptions produce large amounts of sulphate, which may be deposited, on peatlands. This suggests the possibility that
volcanic impacts may affect the balance between methanogens and sulphate reducing bacteria in peatlands, effecting methane flux. Stevenson et al. (2003) suggest that large eruptions such as Laki 1783 may be of sufficient magnitude to substantially suppress methane flux. This suppression may be of sufficient magnitude to have climatic consequences, potentially reinforcing volcano-induced climatic cooling. Impacts could potentially last years to decades. Peatlands may therefore form a secondary level of the volcano-climate system.

The chemical impact of tephra and tephra leachates on peatlands

Tephra contains a variety of elements both contained within the glass and adsorbed on its surface. Elements may be released both on initial contact with water and through longer term leaching. Although it appears that tephra is well preserved in peatlands and has undergone minimal geochemical change over the late Holocene (Dugmore et al. 1992), it has been speculated that very small tephra shards (<2μm) may be rapidly dissolved in lake waters, similar process may also occur in peat waters (Eastwood et al. 2002). The quantity of adsorbed compounds may increase with increasing distance from source and with a decreasing tephra particle size. The elements initially released by tephra leaching most commonly include Cl, S, Na, Ca, K, and Mg (Smith et al. 1983 and references therein). In lakes exposed to proximal volcanic action drastic changes in lake water chemistry have been noticed with large increases in many elements (Wissmar et al. 1981). In peatlands, leachates from simulated tephra deposition have been noted to have detectable impacts on pore water chemistry (Hotes et al. 2004). Hodder et al. (1991) discussed evidence for enhanced Si, Fe, Mg and Ca in pore-waters adjacent to tephra layers preserved in peat. In an oligotrophic system such as a peatland, these inputs could provide nutrients which are in short supply, potentially encouraging plant growth. However peatland plant growth is primarily limited by the availability of macronutrients (N, P and K) which with the possible exception of K will not be extensively supplied by tephra. Increased supply of Ca may even reduce the growth of Sphagnum (Clymo & Hayward 1982). Tephra leachates may also contain elements such as Zn, Cu, Cd, Pb and Ba that may be toxic to some organisms (Smith et al. 1983).
Anthropogenic metal pollutants have been suggested to have caused damage to peatland bryophytes in northern England (Gorham et al. 1987b). The potential for tephra leachates to have impacts on peatlands (either beneficial or detrimental) will depend on the quantity and composition of tephra, the extent of leaching and the bioavailability of these elements.

Summary- direct volcanic impacts on peatlands

The impact of volcanic events on peatlands is uncertain and may arise through the physical impact of tephra, changes in hydrology, the impact of volcanic gases and precipitation and the effects of tephra leachates. Impacts may depend on the quantity of tephra deposited, the structure and vegetation of the site and the season of deposition, particularly with respect to snow cover.
1.3 VOLCANIC IMPACTS ON CLIMATE

1.3.1 Volcano-climate effects: mechanisms of impact and modes of response

As well as affecting the earth's surface volcanic eruptions may also affect the atmosphere. Large eruptions can modify climate around the globe, producing impacts in areas at extreme distance from the volcanic source. The idea that volcanic impacts may have the power to affect climate evolved over 200 years ago. Following recent large eruptions it is becoming clear that significant climatic changes may follow these events. However, the scale of these impacts and the processes involved are still inadequately understood—this is due to a combination of not enough research and the problems with many of the methods so far employed. I will initially consider the mechanisms by which volcanoes may affect climate before moving on to describe the methods that can be used to investigate these effects.

Initial research suggested that climate could be changed by the emission of volcanic dust. In the atmosphere, this dust would reflect solar radiation, decreasing the amount reaching the earth's surface and therefore reducing surface temperatures. More recent studies have shown that volcanic dust only remains in the atmosphere for a short period of time and therefore produces very little impact on climate. Climatic impacts are however produced by volcanic gases. These gases combine with water forming aerosols in the upper atmosphere. It is these aerosols that reflect solar radiation and therefore produce a climatic cooling.

Gases produced in volcanic eruptions include a variety of sulphurous compounds, in particular hydrogen sulphide and sulphur dioxide. Large explosive eruptions inject these gases into the stratosphere where they are converted into sulphuric acid aerosols by combination with water. These aerosol particles are generally efficient scatterers but only weak absorbers of radiation at solar wavelengths. Therefore volcanic aerosols usually serve to increase albedo leading to reflection of solar insolation and global tropospheric cooling. In the 1991 Pinatubo eruption 30 Tg of aerosols were ejected and albedo was increased by up to 20% in cloud-free regions. This effect is dependent on the aerosol particle size, large particles may give increased absorption of terrestrial radiation producing 'greenhouse' warming (McCormick et al. 1995). Aerosol production may also
affect the albedo of clouds, an increase in aerosols means that more condensation nucleii are available for cloud formation. This serves to decrease the mean size of cloud particles, leading to more efficient scattering and an increase in albedo. The most climatically effective eruptions are those at subduction zones where the magmas are oxidized and have high water contents. The oxidised state of the magmas allows crystallization of anhydrite rather than iron sulphide leading to sulphate rather than sulphide magmas. This in turn increases their ability to store sulphur and transport it to the surface where explosive eruptions may propel it into the stratosphere (Luhr 1991). The climatic impact of eruptions is not directly dependent on the overall size of the eruption but is dependent on the amount of sulphur emitted. The relatively small but sulphur-rich eruptions of Mt Agung (1963) and El Chichon (1982) both had affects which exceeded larger but less sulphur rich eruptions (Rampino & Self 1984)

The 1991 Pinatubo eruption produced a change in albedo which exceeded the positive ‘greenhouse effect’ forcing for much of 1992 and into 1993. This resulted in a 1992 mean tropospheric temperature reduction of 0.2°C, when accounted for ENSO this anomaly is more than 0.7°C (McCormick et al. 1995). Tree ring evidence suggests that over the Holocene a typical post-eruption cooling following a significant event would be in the order of a 1°C temperature reduction for up to 2yrs (Scuderi 1990, Gervais & MacDonald 2001).

Methods for investigating volcano-climate effects

The question of volcanic impacts on climate is a controversial one. A variety of lines of evidence have been pursued to investigate the issue including the analysis of long-term meteorological records, the use of historic descriptions, palaeo-climatic records, direct observation of contemporary eruptions and volcano-climate models (Begét et al. 1993). In order to demonstrate the potential utility of new methods for investigating this question I will briefly discuss the advantages and limitations of the existing methods.
1.3.2 Near-Contemporary Methods

Remote sensing of Recent Eruptions

A large proportion of current knowledge about the impact of volcanoes on climate comes from direct observations of volcanic plumes, their distribution in the atmosphere, volcanic aerosol production and ensuing climatic consequences. The advent of satellite-based remote sensing technology has particularly contributed, monitoring of the impacts of the 1991 Pinatubo eruption by the SAGE and UARS instruments provided the first unambiguous proof that volcanic aerosol forcing has the power to effect climate (Minnis et al. 1993, Stenchikov et al. 1998). Satellite monitoring allowed detailed understanding of the climatic aftermath by monitoring of stratospheric, tropospheric and ocean temperatures (e.g. Sutton & Chiswell 1996). The satellite based Total Ozone Mapping Spectrometer (TOMS) showed unusual ozone depletion reflected as increased surface UV levels (Bluth et al. 1992, Robock 2002). Ground based lidar instruments have also been used to monitor stratospheric optical depths, a key variable in determining climatic consequences (McCormick et al. 1978, Rampino & Self 1984, Saxena et al. 1997, Niranjan et al. 1999). Furthermore, remote sensing allows infrared monitoring of volcanoes to monitor and even predict eruptive activity. This may allow improved emergency management as well as better monitoring of the terrestrial and atmospheric impacts of eruptions. The obvious key limitation with the use of remote sensing data to assess the volcano-climate system is the extremely short time-scale for which these data are available. In this time period there has been a very limited range in size of eruptions and pre-existing climatic modes.

Analysis of Meteorological Records

Potentially the most useful information about the spatial and temporal impacts of volcanoes on climate comes from meteorological records. Studies of this type attempt to relate the timing of volcanic events to meteorological records to isolate a volcanic signal. A key issue with these studies is that the large number of volcanic events means there is almost always one that could be associated with any climatic change. There is therefore a
need for some objective criteria to define which eruptions are likely to have climatic consequences. This has been carried out using volcanic chronologies, principally the Dust Veil Index (DVI; Lamb 1970) and the Volcanic Explosivity Index (VEI; Newhall & Self 1982). These indices have several problems for climatic studies; most severe of these is that in both indices the key criterion is the volume of material produced. We now know that volcanic impacts on climate are due to volcanic aerosols rather than volcanic dust, the size of a volcanic eruption provides a poor proxy for volcanic sulphur production. Eruptions identified by these criteria may not therefore be those that are likely to produce the greatest effects (Self et al. 1981, Rampino & Self 1982). There are also problems with the formulation of the indices and the largely inadequate data upon which they are based. The key problem with this approach is that it is virtually impossible to obtain all the required information on sulphur content, aerosols and explosivity for historic eruptions (Rampino & Self 1982).

Statistical analysis of meteorological data attempts to clarify the volcanic signal by averaging out features not common to the individual events which are assumed to be caused by non-volcanic factors and can be considered as noise (Kelly & Sear 1984, Sear et al. 1987). Problems can arise with the approach used in some studies such as the use of long-term averages, which may give an oversimplified impression of the data (Angell & Koshover 1985, Kelly & Sear 1984). Numerous studies of meteorological records from around the world have suggested a range of results for the scale and time of any volcanic-induced cooling. Estimates for the mean volcanic-induced cooling following a large eruption range from 0.2-0.3°C for the following year to a cooling of up to 0.4°C over two years (Mass & Schneider 1977, Self et al. 1981, Sear et al. 1987). Angell & Korshover (1985) suggested that climatic perturbations may even last as long as five years after an eruption. Studies also disagree over when the maximum cooling is likely to occur with estimates between the second month and the following year (Sear et al. 1987, Self et al. 1981, Bradley 1988). Bradley (1988) suggested that summer and autumn temperature anomalies are more likely to be volcanic related than winter and spring anomalies. Studies also disagree about the impacts of specific large recent eruptions. The question of climatic cooling in much of Europe and North America in 1816 ('the year without a summer') following the Tambora eruption in 1815 is a particularly vexed one. Volcanic-
induced cooling has long been suggested as the cause of this event (Stommel & Stommel 1979). However, statistical work on the meteorological record suggested that the weather was already cooling in 1815 prior to the eruption. It has been suggested that the cause of this cooling may be natural climatic cycles (Mass & Portman 1989).

The analysis of meteorological records is limited by several factors including the short length and spatial bias of meteorological records, the limited knowledge of volcanic histories and problems with some of the methods which have been used (Bradley 1988). Even at their most effective, these methods cannot prove a physical link between the eruption and climate; they can merely suggest a strong possibility that one may be present (Sear et al 1987). Nevertheless, meteorological records do have the potential to produce the most useable results about the scale and spatial pattern of climatic impacts over the last 2-300 years.

Volcano-climate modeling

Volcano-climate models attempt to predict the climatic response to volcanic eruptions according to physical laws. Models have the great advantage that we do not need to wait for a large volcanic eruption to see what the effects might be. Models allow repeated simulations with a variety of starting conditions to determine a range of potential outcomes according to conditions. Models can also add to knowledge about the system under investigation by highlighting sensitivities and susceptibilities (Baldwin et al. 1976, Pollack et al. 1976). Models have been developed to study various aspects of the volcano-climate system including plume dynamics of the eruption column, the chemical processes of the stratospheric aerosol, the effects of this on solar insolation and consequent impacts on terrestrial, atmospheric and ocean temperatures (Sutton & Chiswell 1996, Langmann et al. 1997, Timmreck et al. 1997). There is also the potential for volcano-climate models to be linked in to global climate models (GCMs; eg. Stenchikov et al. 1998), these can in turn be linked in to models of vegetation and ice-caps allowing possible feedbacks to be investigated.

Climate models are still far from reaching their full potential. There has been a shortage of work on coupling models of different aspects of the volcano-climate system
together. This is likely to reduce the effectiveness of models, particularly when considering feedbacks between different parts of the system. Modelling is a complicated, time-consuming and expensive process. Models also require data to allow them to be calibrated and parameterised; this calibration data is only available for recent eruptions such as the 1982 eruption of El Chichón, the 1991 eruption of Pinatubo and to a lesser extent Mount Agung in 1963 (Hansen et al. 1978). These were low latitude eruptions of comparatively small magnitude and may therefore not be good models for larger or higher latitude eruptions. Physically-based models are only as good as the science that they are based on. If the rules the model works by are incorrect then the results will be incorrect and misleading. Furthermore, there is also inevitable error in the model structure. Climate is an inherently complex and chaotic system, it is impossible that any model will ever be able to fully characterize the full range of possibilities.

One of the largest volcanic eruptions this century was that of Pinatubo in the Philippines in 1991. This eruption provided an opportunity to test the effectiveness of climate models in predicting a response to forcing by stratospheric aerosols. The accuracy of predictions was variable with some studies predicting a more lagged response to the eruption than was actually observed. However, the spatial pattern of climatic response was generally well predicted (Hansen et al. 1992, Graf et al. 1993). Particular problems in prediction of impacts of Pinatubo occurred due to its coincidence with an El Niño event, complicating modelling scenarios (Self et al. 1999).

1.3.3 Palaeo-records

Much current knowledge about the volcano-climate system comes from monitoring, modelling and instrumental records for the recent past. Over this time-scale there has been a limited number of eruptions and a restricted range of size and type of volcanic eruption and pre-existing climatic modes. Therefore to determine the full variability in the volcano-climate system it is necessary to employ methods which work on a longer time-scale through the Holocene and beyond (Zielinski 2000). These methods are indirect (proxy) records of volcanism and climate; which means that their
interpretation is more complicated. A full consideration of these methods is necessary to demonstrate the requirement for developing new methods.

**Historical & Archaeological sources of evidence**

Historical & Archaeological records of past volcanism can add significantly to our knowledge of volcanoes and their impacts. This can include information on the age and location of eruptions and their impacts on the human and natural environment. As has been discussed previously, chronologies of volcanic eruptions are essential to investigating their impacts. Historical accounts can provide information from both proximal (eg. Hayakawa & Nakajima 1998) and distal regions (eg. Stothers & Rampino 1983). Where historical accounts do not exist, archaeological evidence from affected settlements can provide dates for volcanic events through direct radiocarbon dating or by comparison of artefacts and architectural styles with dated sites (eg. Betancourt 1987, Aitken et al. 1988,). Historical accounts can also provide information on the distribution of volcanic products, which may itself be of climatological interest. Particularly well studied is the 1783 Laki (Iceland) eruption where numerous studies have shown the widespread distribution of volcanic products and consequent impacts on the natural and human environment (Thorarinsson 1979, Sigurdsson 1982, Grattan & Charman 1994, Grattan & Pyatt 1994, Stothers 1996, Grattan & Sadler 1999, Brayshay & Grattan 1999, Grattan et al. 1999, Jacoby et al. 1999).

The usefulness of historical records is limited by their spatial and temporal extent. Long-term volcanic histories have only been obtained from selected areas- principally Mediterranean Europe, the Near East, Japan and China and even at their very longest do not span more than the late Holocene (Stothers & Rampino 1983, Pang et al. 1987, 1988). This arguably leads to a geographic bias, for example Stothers & Rampino (1983) considered that five of the nine largest peaks in the acidity record from 1390BC to 1258AD could be attributed to European eruptions, this would seem an extremely high proportion given the number and climatic effectiveness of European volcanoes. Further uncertainty comes from the difficulty in interpreting ancient texts; accounts of dry fogs, reduced sunlight and dust falls have been commonly taken to indicate volcanic activity
but could conceivably represent other meteorological or solar phenomena (Camuffo & Enzi 1995). Those eruptions that produce notable impacts at ground level and are recorded in historical accounts may not be those with the greatest climatic affects (Grattan & Pyatt 1999). Dating of historical records may be difficult due to the problems of interpreting ancient calendars and the lack of fixed points. Overall, historical records are subjective in interpretation, difficult to date and limited in extent. Due to this uncertainty they are particularly prone to the problems of 'suck-in' and 'smear' when trying to match them to signals in palaeo-records such as ice-core acidity (Baillie 1991).

Ice core records

Records from ice cores can show the presence of volcanic acids in precipitation, potentially revealing the age, magnitude and chemical composition of volcanic eruptions and the distribution of volcanic products (Zielinski 2000). As ice cores record the presence of volcanic acids (as opposed to other volcanic products) they may provide a direct record of the possible climatic effectiveness of past eruptions. These layers may be accurately dated where annual layers are present. The potential of the technique was first demonstrated by Hammer et al. (1980) who showed the presence of acid peaks representing around 40 major volcanic events, in ice cores from Greenland. This study measured the electrical conductivity of the ice, more recent studies have used a higher resolution and techniques such as liquid conductivity, $\text{H}^+$ concentration, $\text{SO}_4^{2-}$ concentration and total salt measurements to separate out non-volcanic acids and reveal a greater number of eruptions (Herron 1982, Legrand & Delmas 1987, Zielinski et al. 1994, Zielinski 2000). Key findings from this work include revealing the scale of the 1783 Laki eruption, suggesting possible combined impacts from the 1883 Krakatoa and 1886 Tarawera eruptions and showing a large eruption of unknown source in 1259AD (Clausen et al. 1987, Langway et al. 1988, Palais et al. 1992, Delmas et al. 1992, Legrand & Delmas 1987). Ice cores can also reveal changes in temperature through the ratio of the oxygen isotopes $\delta^{18}\text{O}$ and $\delta^{16}\text{O}$ (Nijampukar et al. 2002, Jouzel et al. 1993); these records can be related to acidity records to suggest volcanic impacts on climate. These methods have been used to suggest volcanic impacts on climate around 70ka BP.
caused by the Toba eruption (Zielinski 2000), around 17.5ka BP (Hammer et al. 1997) and possibly even triggering the last glaciation (Zielinski et al. 1996). Most recently, mineral particles including volcanic tephra have been found in ice cores (Betzer et al. 1988). Tephra allows acidity layers to be identified to a source volcano and can be compared to other tephra records to investigate the scale of an eruption (Zielinski et al. 1995, Zielinski & Germani 1998, Manning 1998, Smellie 1999, Eastwood et al. 2004, Pearce et al. 2004).

Ice core records are limited in several respects. Suitable coring sites only exist in a small number of areas; the expense of ice core drilling programs means that the number of long cores obtained remains small and very few of these are from low latitudes (Thompson et al. 1986, 1998). The acids deposited in an ice core do not necessarily provide an accurate indication of the volume of acids produced by a volcano and will be heavily influenced by proximity and prevailing meteorological conditions, leading to a bias towards high latitude eruptions. Comparison of records from the Arctic and Antarctic may help to identify the largest eruptions and remove this geographic bias (Legrand & Delmas 1987, Langway et al. 1988). A further complication is that acids preserved in an ice core represent acids present in the troposphere and may therefore not be a good representation of those in the stratosphere. There are also continuing problems with isolating volcanic events from a variable non-volcanic acidity (Crowley et al. 1993). Despite these issues ice core records are highly valuable for identifying climatically effective eruptions, and are particularly valuable for identifying pre-Holocene events.

Dendrochronology and Dendroclimatolog

Volcanic impacts on climate and the environment may be revealed by dendrochronology. As most trees grow they produce a ring annually with lateral growth, this growth and therefore ring width may depend on climate allowing climatic reconstruction. This pattern of wide and narrow rings may be comparable across a large area allowing a master sequence to be compiled from numerous trees; individual trees can be dated by comparison to this sequence. Long dendrochronological sequences have

Trees may be affected by the proximal (lava, pyroclastic flows, lahars) and distal (tephra fall, gases, acid precipitation, climate change) impacts of volcanic activity. Volcanic events may be dated by cross-dating preserved wood in volcanic deposits, by dating trees growing on volcanic deposits or by investigating narrow tree rings in preserved wood (Brantley et al. 1986, Wiles et al. 1996). Tephra deposition, volcanic gases, volcanic precipitation and volcanic induced climate change will stress a tree leading to reduced growth and a narrow ring (Yamaguchi 1993). Extreme distal impacts of volcanism was first shown in tree ring studies by LaMarche & Hirschboek (1984) who located ‘frost rings’ in Californian Bristlecone pines which they interpreted as representing unusual growing season frosts caused by the climatic impact of the 17th century BC eruption of Santorini (Thera; see also Baillie & Munro 1988). Other studies have applied similar methods to investigate the impacts of the Hekla 4 eruption (Baillie 1995), 15th Century AD eruptions of Mt. St. Helens (Yamaguchi 1985) and the Laacher-See eruption (Friedrich et al 1999) among others (Kaiser & Kaiser-Bernhard 1987, Schweingruber 1988, Baillie 1994, Briffa et al. 1998, Jacoby et al. 1999, Gervais & MacDonald 2001). Tree ring data has also been used to investigate the effects of metal pollution and acidification (Watmough & Hutchison 1996, Stewart et al 1991, Legge et al 1984), it is interesting to wonder if these techniques could be used to investigate the impacts of tephra and volcanic acids on plants.

There are several important issues with tree ring studies of volcanic impacts; perhaps the most important of these is the mode of response. Many studies have assumed a climatic mechanism of impact but an alternative explanation is that impacts are due to acid precipitation, this has been little considered (Kaiser & Kaiser-Bernhard 1987, Grattan et al. 1999). A further issue is the possibility for narrow rings to be caused by other processes such as competition, parasites, disease and fire, these events could be difficult to differentiate from volcanic events (Yadov 1992, 1993, Yamaguchi et al. 1993, Gervais & MacDonald 2001). The climatic records produced by tree ring width measurements are also a composite record and are unable to differentiate temperature and precipitation changes potentially limiting their usefulness. Tree-ring studies have
provided valuable information on the timing and impacts of volcanic impacts. However, the issues with mode of impact (direct vs. indirect) and the problem of differentiating volcanic from non-volcanic impacts may be serious constraints. The application of the technique is also limited by the availability of suitable wood for the non-recent past.

Other methods

Studies in several other environments have also suggested volcano-climate effects. In lake sediments, several studies have investigated the impact of volcanic events. Impacts may be noted through changes to pH and silica supply (Lotter & Birks 1993, Barker et al. 2000, Eastwood et al. 2002). In general these direct impacts seem to predominate over any climatic signal that may be present. An interesting exception to this is the study of Lamoureux et al. (2001) looking at varved sediments in the Canadian Arctic. Results showed a significant correlation between increased summer rainfall events in the sedimentary record and eruptions recorded in ice-cores. This is particularly interesting as it shows a rainfall response rather than a temperature (or combination) response as indicated by the majority of other proxy records. Proxy-records in other environments have also suggested a volcano-climate response although these have received little work. Crowley et al. (1997) found a reasonable agreement between years following an eruption and cooler sea surface temperatures indicated by the $^{18}$O record from Corals in New Caledonia. Baker et al. (1995) have suggested that a signal from the Icelandic Hekla-3 eruption may be detectable in a Scottish speleothem, although this finding is debatable (Dugmore et al. 1999).

1.3.4 Summary

These methods all have specific associated problems. Remote sensing can provide the most detailed information about how and why volcanoes affect climate but is highly restricted by the limited number and scale of recent eruptions. Meteorological records can provide highly useful information of the spatial variability and duration of volcanic impacts but are very limited in extent. Modelling approaches allow repeated scenario
tests but are limited by the availability of parameterisation information and an inevitable over-simplification in model structure. Historical approaches can provide valuable information on volcanic chronologies and impacts but are inherently subjective and open to interpretation. Ice core studies provide perhaps the most useful palaeoenvironmental method for investigating volcanic impacts as they show direct evidence of volcanic acids. However there are limitations due to the number of available studies, a geographical bias in eruption representation and in most studies the lack of a direct climatic record. Tree ring records can provide evidence of volcanic impacts but there are complications in determining the mode of impact and possible complications due to the similarity of various affects.

That volcanoes can affect climate is well known. What is more difficult is determining the scale of impacts from a specific eruption. The methods that have been used to date all have some associated problems. There is therefore the potential for new methods to add to the debate. Peatlands can provide palaeoclimatic records; it is therefore possible that peatland palaeoecology may provide a new method to investigate volcanic impacts on climate. Peatlands might be affected by volcanic eruptions through two pathways. First, the direct impact of volcanic products on peatlands through physical, chemical and hydrological changes. Second, through the impact of volcanoes on climate consequently producing changes in mire surface wetness. The primary theme of this thesis is investigating and differentiating these processes.
1.4 PEATLANDS AND PALAEOCLIMATES

1.4.1 Introduction

The development of peatlands is closely linked to climate. By analyzing material preserved in peat it is possible to reconstruct a changing climate. The palaeoclimatological study of peatlands concentrates on the use of water-shedding, ombrotrophic bogs. These mires are effectively isolated from the surrounding environment and can maintain their water table above that of the surrounding soil. They are considered to be directly coupled to the atmosphere; their surface wetness is determined by the balance between precipitation and evapo-transpiration (plus seepage). Bog-surface wetness therefore provides an integrated measure showing how warm/dry or cold/wet the climate is. As these bogs only receive nutrient inputs through the atmosphere they are highly nutrient poor (oligotrophic). This oligotrophy leads to specialized vegetation, dominated by species of *Sphagnum*. Due to the waterlogged conditions, oligotrophy and acidity of these systems, there is little microbial action in the lower regions of the peat. Therefore, once material passes from the surface of the bog (acrotelm) into that area which is permanently below the water table (catotelm), there is little further degradation of organic material. This leads to the accumulation of organic sediments over long periods of time. Temperate peat-bog sequences may span over 10,000 years and 10 m of peat (Birks & Birks 1980, Barber 1993, Blackford 1993, Roos-Barraclough *et al.* 2004).

Peat-bog paleoecology utilizes these archives in two ways; firstly by examining the composition of the peat. Peat contains the sub-fossil remains of the plants and organisms which were living on and within the peat when it was part of the acrotelm. Analysis of this material and the physical properties of the peat may yield important paleoecological information about the past environment of the peatland. Secondly, bogs trap and preserve atmospheric particles within their structure. Due to the anoxic and low-energy environment these particles will be preserved and will remain in their stratigraphic context. Therefore bogs may also retain information about processes in their wider
environment. A large number of methods have been used to investigate past environmental change and the dating of these records; these are outlined in Table 1.1.

Peatland stratigraphy has been used as a source of proxy climatic data since the 19th century and was perhaps the most widespread method prior to the advent of pollen analysis (Blackford 1993). Darker layers of highly decomposed peat, sometime with tree stumps were taken to indicate a drier bog surface when pine or birch trees were able to establish on the bog surface. Layers of lighter coloured *Sphagnum* peat were taken as indicating wetter surface conditions and faster bog growth. Studies of this peat bog stratigraphy led to the development and acceptance of the Blytt-Sernander scheme of five stages of post-glacial climate. This scheme has now been largely discounted as over-simplistic (Birks & Birks 1980, Lowe & Walker 1997).

Peatlands allow palaeoclimatic reconstruction by analysis of preserved material in peat and interpreting results with regard to the hydrological preferences of the species recovered. This research relies on four key assumptions:

1. That peatland surface wetness is directly linked to climate
2. That peatland organisms are directly affected by peatland surface wetness
3. That organisms preserved in peat are an accurate representation of those living on the mire surface in the past
4. That it is possible to accurately date this material

Table 1.1 Sources of palaeoenvironmental evidence from peatlands and palaeoenvironmental applications (Adapted from Charman 2002)

<table>
<thead>
<tr>
<th>Evidence</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratigraphy</td>
<td>Major environmental changes</td>
</tr>
<tr>
<td>Pollen, Fungi and Spores</td>
<td>Vegetation changes and human impacts on vegetation-local and regional. Also as time-markers.</td>
</tr>
<tr>
<td>Plant macrofossils</td>
<td>Peatland plant changes (climate change)</td>
</tr>
<tr>
<td>Tree stumps/remains</td>
<td>Dendrochronology/Dendroclimatology</td>
</tr>
<tr>
<td>Charcoal</td>
<td>Local and regional fire histories</td>
</tr>
<tr>
<td>Diatoms and other algae</td>
<td>Hydrological changes</td>
</tr>
<tr>
<td>Testate amoebae</td>
<td>Hydrological conditions (climate change)</td>
</tr>
<tr>
<td>Chironomids</td>
<td>Palaeo-temperature changes</td>
</tr>
<tr>
<td>Coleoptera</td>
<td>Palaeo-temperature changes</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>Mineral inputs (past storminess)</td>
</tr>
<tr>
<td>Magnetic Susceptibility</td>
<td>Ferromagnetic mineral content including tephra location</td>
</tr>
<tr>
<td>X-radiography</td>
<td>Locating tephra and other mineral layers</td>
</tr>
<tr>
<td>Radar &amp; geophysical survey</td>
<td>Morphology and general stratigraphy</td>
</tr>
<tr>
<td>techniques</td>
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<tr>
<td>Bulk density</td>
<td>Accumulation rates, palaeohydrology?</td>
</tr>
<tr>
<td>Humification</td>
<td>Peat decay, palaeohydrology</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>Chemical changes, regional and global human impacts</td>
</tr>
<tr>
<td>Biomarkers</td>
<td>Palaeoclimate</td>
</tr>
<tr>
<td>Isotopes (C, H, O)</td>
<td>Water sources, palaeoclimate, balance between C3-C4 plants</td>
</tr>
<tr>
<td>Luminescence and Near infrared spectra</td>
<td>Humification, tephra location</td>
</tr>
<tr>
<td>$^{14}$C, $^{210}$Pb, $^{241}$Am, $^{137}$Cs, $^{3}$H</td>
<td>Dating sediments</td>
</tr>
<tr>
<td>Tephra</td>
<td>Time-marker</td>
</tr>
<tr>
<td>Spheroidal Carbonaceous</td>
<td>Time-markers (recent past)</td>
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<tr>
<td>Particles</td>
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<tr>
<td>Moss growth increments</td>
<td>Recent peat accumulation</td>
</tr>
<tr>
<td>Pollen density</td>
<td>Peat accumulation rate</td>
</tr>
<tr>
<td>Peat accumulation models</td>
<td>Peat accumulation rate</td>
</tr>
</tbody>
</table>

Perhaps the greatest advantage of peatlands as sources of palaeoclimatic information is their geographical extent. Peatlands cover perhaps 400 million hectares of the Earth’s surface throughout the high northern and southern latitudes. A large proportion of these peatlands are capable of producing useable proxy-climatic records spanning much of the Holocene. Peatlands are also relatively easy to study; to extract a core from a peatland is a simple operation using manual equipment; this process can therefore be repeated numerous times. When compared to the availability of long ice
cores and early Holocene preserved wood or historical records, the advantages in availability and accessibility of peatland archives are clear. This therefore gives huge potential for developing globally integrated records reconstructing the spatial as well as temporal extent of Holocene climatic change.

1.4.2 Problems with the record

As with all palaeo-records, peat bog palaeoecology faces some problems and limiting factors. Perhaps the most historically persistent of these is the possibility that the record may be primarily influenced by autogenic processes. The early promise in peatland palaeoecology was severely limited by the advent of the theory of cyclic regeneration proposed by Osvald (1923). It was suggested that bog growth proceeded through cyclical replacement of hummock and pool microforms on the bog surface. Deposition of material would occur faster in pools than on hummocks. The open water of a pool would be encroached upon by aquatic Sphagna which would encourage deposition eventually allowing hummock forming Sphagnum species to establish themselves, which would in turn be replaced by species like Calluna and Rhacomitrium. This hummock would then cease growing, eventually being over-taken by new hummocks to become a pool again. It was accepted that climate could have an impact on development, but that this was only discernible by the presence of 'Recurrence Surfaces', the gross change between a layer of dark, humified peat, overlain by lighter, less humified peat (Birks & Birks 1980, Barber, 1993). This theory therefore greatly limited the potential of peat bogs as a source of proxy climate data. The theory effectively persisted for over fifty years despite a lack of studies in support. Walker & Walker (1961) cast the first serious doubt on its validity when in a study of eight Irish bogs they found little evidence for the regeneration complex. This doubt was added to by Aaby (1976) who found that a 5500 year humification record appeared to show a good climatic signal and that hummocks tended to persist in time rather than be replaced by pools. Barber (1981) conclusively disproved the theory by detailed analysis of stratigraphy and macrofossils at Bolton Fell Moss, Cumbria. This has been backed up by further work since such as that of Svensson (1988). It therefore seems that peat bogs may indeed contain good climatic signals.
However the possibility remains that autogenic forcing may still have some role to play in bog development, this is poorly understood (Tolonen 1986, Barber 1993, Muller et al. 2003). Further problems with the record are posed due to the possibility that bog surface-wetness (the prime paleoecological variable) may be altered by other external processes apart from climate. It seems probable that anthropogenic changes such as peat cutting, burning, drainage and grazing may also produce changes in the palaeo-record, which could be misinterpreted as a climatic signal (Blackford 2000, Roos-Barraclough et al. 2004).

To date, the majority of peatland palaeoecological studies have reconstructed peatland surface wetness solely in qualitative terms. This is of limited use for climate reconstruction, particularly when trying to compare between sites and with the results of other methods. More recent methods now make it possible to quantitatively reconstruct changes in peatland surface wetness (Depth to Water Table; DWT). This is a composite variable which in ombrotrophic peatlands represents the balance of evapo-transpiration and precipitation. It is therefore dependent on temperature as well as precipitation, palaeoecological reconstructions are largely inadequate to differentiate the two. There has been relatively little research investigating the precise climatic controls on peatland water tables and how this varies between sites (Charman et al. 2004). Additional problems are posed by the dating of peatland palaeoecological records. Peat provides a good medium for radiocarbon dating, however the cost and sample size requirements of radiocarbon mean that the age-depth models used in many studies are based on a small number of widely spaced dates. These poor age-depth models impair accurate climatic reconstruction and comparison between studies. Despite these limitations, peatland palaeoclimatology has great potential to add considerably to our knowledge of late Holocene climate change.
1.5 SCOPE OF THIS THESIS

The previous sections have shown that volcanoes can have environmental impacts on both a local and global scale. Peatlands are sensitive to environmental change and may be affected by volcanoes through various mechanisms.

The central research question of this thesis is:
'Can volcanic activity affect the functioning of peatlands, and if so how do these impacts occur?'

The research proceeded with two working hypotheses to explain any impacts:
A) Impacts are due to the direct impact of volcanic products falling on the peatland.
B) Impacts are due to a volcanic impact on climate, represented as a change in peatland surface wetness.

The research integrates several approaches:

1) Tephrochronological techniques were used to locate tephra layers in peatlands. It is these tephra layers which provide the direct evidence of volcanic events in the peatland record.
2) The primary approach used is palaeoecological studies across tephra layers. Techniques developed for peatland palaeoclimatic studies are applied at high resolution across tephra layers. These techniques can demonstrate peatland surface wetness changes but are also likely to respond to direct volcanic impacts. The palaeoecological record across several visible and microscopic tephra layers is investigated using a multi-proxy approach and the records are dated using radiocarbon.
3) One of the key issues with the study is determining how the direct impacts of volcanic products on peatlands would be represented in the palaeoecological record. Understanding this is crucial to separating direct from indirect causes of
any changes represented in the palaeoecological record. To investigate this an ecological experiment was carried out, applying tephra and acids to a peatland. Impacts were monitored using the same techniques applied in the palaeoecological studies.

4) One of the key methods used in the palaeoecological studies is testate amoebae analysis. To allow interpretation of the record it is necessary to gain some understanding of the modern ecology of these microorganisms. Testate amoebae ecology has been investigated quantitatively deriving a species-environment (transfer function) model. This model allows quantitative reconstruction of peatland surface wetness and pH.

5) The palaeoecological studies rely on precisely relating the location of the tephra layer to any changes in the palaeoecological record. This linkage may be imperilled if tephra moves through the peat after deposition. To investigate this, experiments on tephra taphonomy were carried out in conjunction with the ecological experiment described above.

This combined approach should give a more complete understanding of the processes occurring. The palaeoecological studies should establish if any volcanic impacts on peatlands have occurred in the past. The ecological experiment will test a range of scenarios to try to determine the modes of impact. The transfer function and taphonomy experiments will enable informed interpretation of the results of the palaeoecological study. Impacts may be possible through mechanisms such as a volcanic induced climate change, the physical impact of tephra, the impact of volcanic acids, chemicals adhering to tephra and tephra leachates. Results may reveal have implications for peatland conservation and utilisation and could reveal volcanic impacts on climate, potentially adding to our understanding of these processes.
CHAPTER 2. TESTATE AMOEBAE TRANSFER FUNCTION

2.1 INTRODUCTION

One of the key methods used in the ecological and palaeoecological studies in this thesis is testate amoebae analysis. Testate amoebae are unicellular microorganisms characterised by a solid ‘test’ enclosing the cytoplasm. They are also known variously as rhizopods, arcellaceans and thecamoebians (Charman 1999). The group falls within the superclass Rhizopoda however the systematics of the group is complex. Charman (1999) considered the group to contain those species of the classes Lobosea and Filosea which form a test. As such, the group is a rather artificial division.

The taxonomy of the group is complicated as asexual reproduction appears to be the norm making a biological species concept essentially meaningless. Therefore, morpho-species, primarily based on the characteristics of the test are widely acknowledged. Taxonomy in the fossil record is particularly complicated as many of the defining characteristics such as the pseudopodia are not preserved. Morpho-species based on the fossil record may therefore group many species in death, which are separable in life.

Testate amoebae have strong preferences for environmental conditions; they therefore make excellent indicator species. Testate amoebae species are widely found in most aquatic environments and have been studied in peatland (e.g. Charman et al. 2000), lake (e.g. Patterson & Kumar 2002) and salt-marsh sediments (e.g. Charman et al. 1998). They are found in the majority of the world’s peatlands and remain identifiable for millennia. Testate amoebae have consequently been a component of palaeoecological studies since early in the 20th century (Steinecke 1927, Harnisch 1927). Testate amoebae will be an important proxy-record in this study; this is discussed more in section 5.5.

Initial testate amoebae ecological research looked at determining the autecology of species or grouping species into community assemblages (Paulson 1952, Hoogenraad & DeGroot 1979, Beyens et al. 1986, 1990, Warner 1987, Trappeniers et al. 1999, 2002). More recently, increasing research has concentrated on quantifying species-environment relationships. Ordination techniques have been used to examine the relationships and...
modeling techniques to allow quantitative reconstruction from the palaeoecological record. Initial species-environment modelling used simple weighted averaging techniques (Warner & Charman 1994), however recent developments in statistical analysis and software (Birks 1995) now allow a wider range of regression models to be formulated and tested (e.g. Woodland 1996, Woodland et al. 1998, Mitchell et al. 1999). Results obtained with one of these models allow prediction of palaeo-water tables to within +/- 3.9cm (Woodland et al. 1998). This method therefore has great potential for quantifying and improving the accuracy of climate reconstructions.

A number of studies have now been undertaken to quantify testate amoebae-environment relationships for sites around the world including New Zealand (Charman 1997, Wilmshurst et al. 2003), the UK (Woodland et al. 1998), Michigan USA (Booth 2001, 2002), Western Russia (Bobrov et al. 1999), France & Switzerland (Mitchell et al. 1999), Finland (Tolonen et al. 1994), Poland (Lamentowicz & Mitchell in press) and Canada (Charman & Warner 1992, Warner & Charman 1994, Charman & Warner 1997). These have been used in several attempts at quantitative reconstruction of Holocene climatic change (Charman & Hendon 2000, Mitchell et al. 2001, Hendon et al. 2001, Charman et al. 2001, Wilmshurst et al. 2003).

Despite the generally cosmopolitan distribution of peatland testate amoebae species (Finlay et al. 2001), it is possible that their ecological preferences differ among regions, especially if those regions differ with respect to peatland type or climate. In this study, sites in Alaska are used in the palaeoecological research, there is no existing transfer function for Alaska. The study of testate amoebae ecology in Alaska and the development of new transfer function models based on this data are therefore a prerequisite to their use in palaeoecological studies and will also add to our wider knowledge of testate amoebae ecology and biogeography.

A transfer-function study fulfills several key roles in this project. Most importantly, a transfer function allows interpretation of the palaeo-testate amoebae results in terms of quantifiable variables. A transfer function allows us to determine what a specific community change means in terms of measured environmental variables i.e. a ‘X cm’ water table movement or ‘X unit’ pH change rather than simply ‘a bit wetter’ or ‘a bit more acidic’. Transfer function results may therefore help to distinguish testate
amoebae change induced by changing hydrology, acidity or other factors. Testate amoebae ecology is investigated with regard to two key environmental variables- Depth to Water Table (DWT) and pH. These variables are the primary controls on testate amoebae distributions in peatlands and are also important to investigating and differentiating the impacts of direct or indirect volcanic effects.

2.2 SITES

A series of sites in Southern Alaska was selected for the training set including two sites in which palaeoecological research was carried out (Moose Pass and Sterling). The sites are distributed along a 250 Km North-South transect from the southern Kenai Peninsula to the Susitna River valley in southern Interior Alaska (Fig. 2.1). These sites were selected to represent a range of peatland types from oligotrophic to more mesotrophic, with varying extents of tree cover from tree-less to largely forested, from a mild maritime climate to a cooler and more continental regime and with a large variation in mire size. While few of the mires may be ombrotrophic sensu stricto, none receive significant drainage. It is hoped that with this range of sites, the transfer function developed will be applicable to sites covering a large geographic area- at least as broad as that being considered in this study. Seven sites were sampled for this research:

Kachemak (KC)

This site lies around 59°47′N, 151° 09′W overlooking Kachemak Bay in the southern Kenai Peninsula. The site is at an altitude of around 300m in the hills on the northern side of Kachemak Bay. The site occupies a terrace of around 200x100m. It is bisected by a snowmobile / 4x4 track which heavily disturbs the center of the site. The site is on a slight slope down to the south and clearly receives some degree of drainage from hillsides behind the site. The site is characterized by deep hollows and steep hummocks. The vegetation of the site is sedge-dominated with abundant *Trichophorum caespitosum* and *Sphagnum* spp mostly restricted to hollows.
Fig. 2.1 Sampling sites in South-Central Alaska
Clam Gulch (Kasilof, KSF)

This site lies on the extensive coastal plain of the Western Kenai Peninsula between the towns of Kasilof and Clam Gulch at around 60°14’N, 151° 22’W. The site is a moderately sized peatland, approximately 800 x 250m occupying a shallow basin. When sampled the site was quite wet with three large pools occupying the center of the site, parts of the peatland may be floating on these pools. The site is largely flat with some low hummock and hollow microforms. Vegetation of the site is heavily Sphagnum dominated with E. nigrum, Ledum groenlandicum and Cladonia portentosa on hummocks. The site is largely free of trees with the surrounding Picea woodland extending little beyond the edge.

Ninilchik (NI)

This site lies on the western Kenai Peninsula adjacent to the shore of the Cook Inlet at 60°00’N, 151° 42’W. The site is a large, flat peatland occupying a basin around 500 x 200m. The site is surrounded by coniferous forest but is largely tree free. In common with many peatlands in this region, the site appears to be non-ombrotrophic and may represent the infilling of a lake basin. When sampled, the site was very dry with many plants appearing desiccated and dying. There is some evidence that the site may have experienced anthropogenic disturbance through 4x4 and ATV use. Vegetation of the site includes Sphagnum spp, Empetrum nigrum and sedges. No water table depth measurements are available from this site.

Sterling (ST)

This site lies around 60°31’N, 150° 31’W in the northwestern Kenai Peninsula. The site is large (c.300x200m) and as with other sites may represent lake-infill, the site receives little obvious drainage. The site has more tree cover than other sites sampled on the peninsula, which may represent drier conditions. The site has notable holes in the surface.
and steep hummocks, the vegetation is *Sphagnum* dominated. The site lies in a large flat area with a number of small peatlands and lakes divided by mature conifer forest.

**Moose Pass (MP)**

This site is situated in the steeply glaciated valley of Moose Pass at around 60°30'N, 149°26'W in the northeastern Kenai Peninsula. The site is a small mire, c.100x100m occupying a flatter area in the valley base. There is a slight slope to the north and east within the site. The vegetation of the site is dominated by low hummocks of *Sphagnum* with scattered *Pinus contorta*, the site is surrounded by poorly developed *Picea* forest.

**Houston (HO)**

This site lies within the northern limits of the city of Houston at 61°38'N, 149°51'W. The peatland lies on the eastern edge of the Susitna river floodplain, adjacent to higher ground, which eventually leads to the Talkeetna Mountains. The mire forms part of a large wetland complex covering more than 20 Km² of the valley of the Little Susitna River, a tributary of the Susitna River. The sampled area occupies two adjoining treeless clearings within a region of scrubby *Betula* woodland, approximately 300m from the eastern edge of the site. The vegetation of the sampling area is dominated by *Sphagnum* spp, other species including *L. groenlandicum*, *A. polifolia* and sedges occur on hummocks.

**Sheep Creek (Talkeetna: TL)**

This site is the most northerly of the sites studied here (62°00'N, 150°03'W), the peatland lies approximately 3Km from the eastern bank of the Susitna River, approximately 2Km north of its confluence with Sheep Creek. The mire is extensive and forested in areas. The sampling site occupies an area approximately 200m west of the George Parks Highway. The vegetation of this area consists of scattered *Picea* and *Betula*
with *Sphagnum* dominated lawns and hollows, with sedges *L. groenlandicum* and *E. nigrum* on hummocks.

In addition to the sites sampled specifically for this thesis, data from a further two sites was also included:

**Jigsaw Lake (JL)**

This peatland (60°45'N, 150° 30'W) is adjacent to Jigsaw Lake, an oligotrophic, closed basin lake located within the Kenai National Wildlife Refuge (KNWR). The mire is located in a small cove facing northwest and surrounded by *Picea* forest. The peatland edge floats on the water-body, but most of its surface is approximately 1 m higher than the lake level. The vegetation of this site is dominated by *Sphagnum* spp, *Betula* spp, *Andromeda polifolia*, *Picea mariana*, and *L. groenlandicum*. Testate amoebae samples from this site were analyzed by Keiko Kishaba, University of Alaska, Anchorage.

**Bicentennial Park (BB)**

This peatland is located in the Bicentennial Park of Anchorage, in the foothills of the Chugach Mountains (61°06'N, 149° 44'W). It is composed of two open bodies of water surrounded by a floating peat mat, gradually becoming firmer towards the periphery. The mire is surrounded by upland forest dominated by birch and spruce. At the contact between the upland forest and the peatland is a lagg, with extensive *Sphagnum* cover. The peatland surface is composed of well-developed micro-topography with hummocks, lawns and hollows. The vegetation includes *Sphagnum* spp., *L. groenlandicum*, *Chamaedaphne calyculata*, *Myrica gale* and *Vaccinium* spp. Testate amoebae samples were analyzed by Dr Edward Mitchell, University of Alaska, Anchorage (now at the Swiss Federal Institute of Technology and the Swiss Federal Research Institute, Lausanne).
2.3 METHODS

Initial fieldwork was conducted in April 2003. The study sites were selected and surface samples removed for analysis in the laboratory. To provide some measure of replication, at least three sites from each microform type on the mire surface (hummock, hollow, lawn etc) were sampled; between nine and thirty samples were taken from each site. Samples approximately 5x5x10cm were removed and placed in sealed plastic bags for return to the laboratory. At each sampling site, the surface vegetation was described and a GPS reading taken. To provide an estimate of water table depth variation over the growing season, PVC rods were inserted in the ground at each sampling point following the method of Belyea (1999) and Bragazza (1996). Subsequent fieldwork was conducted in September 2003, additional peat samples were taken and the depth to water table (DWT) measured by digging a small hole and measuring the depth from the surface after at least 30 minutes. The trial with PVC rods was unsuccessful due to disturbance by animals and insufficient length of rods at some sites. Peat pH was measured on the samples taken at the second sampling. A 20 ml volume of each moss sample was placed in a 100 ml beaker. The beakers were filled with distilled water to the 100 ml level and left for one hour with intermittent stirring with a glass rod. The pH was then measured using a Thermo Orion Portable pH/ISE Meter, model 250 A plus.

Testate amoebae were extracted from the surface samples removed in the first fieldwork. In all samples, the dominant moss species was used in the preparation; this was a Sphagnum species in the vast majority of samples. The upper green part of each moss was removed and the section from around 3 to 5cm depth used in the preparation, as this is believed to be most representative of the death assemblage. Testate amoebae sample preparation is based on the method of Hendon & Charman (1997). Moss samples were cut into fine pieces and boiled in distilled water for 10 minutes to release the amoebae. The boiled samples were then filtered at 300 μm and back filtered through a 15μm mesh. The fraction remaining on the 15μm filter was stored in 5ml vials with glycerol. Testate amoebae were identified and counted under light and phase contrast microscope using several identification guides (Deflandre 1929, 1936, Grospietsch 1958,
Corbett 1973, Ogden, 1983, Ogden & Hedley 1980, Lüftnegger et al. 1988, Charman et al. 2000, Clarke 2003). A minimum of 150 individuals was aimed for in counting. Along with testate amoebae, the rotifer *Habrotrocha angusticollis* was also counted and tallied for numerical analysis. The data used for statistical analyses are based on percentages rather than absolute abundances to permit easier comparison with the palaeoecological record. As samples were counted by three different analysts, a conservative taxonomic approach was adopted based on that of Charman et al. (2000).

**Data Analysis**

Several approaches were used to examine the general structure of the data and species-environment relationships. These analyses were carried out using a data-set from which species with less than five occurrences, samples without DWT or pH measurements, and two outlier samples were excluded. Initially a DCA was carried out using log-transformed data to investigate the general data structure. General relationships between testate amoebae communities and both the environmental variables and the sites were examined using Mantel tests. Species-environment relationships were analyzed and quantified using Redundancy Analyses (RDAs). Data was transformed using the Hellinger distance to allow use of RDA rather than CCA. Variance partitioning was carried out to investigate the relative contribution of the sites, environmental variables and unexplained variance. These analyses were carried out by Edward Mitchell and Keiko Kishaba; results are summarized here, full details are presented in Payne et al. (submitted a).

As the RDA showed that there are strong relationships between both pH and DWT and testate amoebae community composition (details are presented in the results), there is therefore a valid basis to relate these properties using species-environment models (transfer functions). As an initial DCA showed the gradients to be long, it was most appropriate to use models based on a unimodal distribution. Linear methods such as partial least squares (PLS) are avoided as these have also been shown to be problematic when used for palaeo-environmental reconstruction with testate amoebae data (Wilmshurst et al. 2003). Three unimodal models are tested here: 1. Weighted Averaging
Testate Amoebae Ecology

(WA), 2. Weighted Average Partial Least Squares (WA-PLS), and 3. Maximum Likelihood (ML).

Weighted averaging (WA) is the simplest of the three models. This technique works on the assumption that a species will be most abundant at its optimum for an environmental variable and therefore it is possible to estimate a species’ optimum by taking an average of the values for an environmental variable at each site the species occurs and weighting this average by the species abundance at each of those sites (Birks 1995). Weighted averaging has been the preferred or only model used in the majority of testate amoebae transfer function studies to date (Charman & Warner 1992, 1997, Mitchell et al. 1999, Warner & Charman 1994, Wilmshurst et al. 2003, Woodland et al. 1998). Weighted averaging has the advantages of being both conceptually and computationally simple. Modifications of WA with tolerance downweighting (WA-Tol) and with both inverse and classical deshrinking were also tested.

Weighted average partial least squares (WA-PLS) is a modified form of WA which is essentially a unimodal equivalent of PLS. It is an improvement over WA in that it takes account of residual correlations in the biological data (Ter Braak & Juggins 1993, Birks 1995). This method has been used in some studies of testate amoebae ecology and found to outperform simple WA (Booth 2001, 2002, Bobrov et al. 1999). The number of components required to produce optimal performance varies between data sets.

Maximum Likelihood (ML) is the most statistically rigorous technique used in this study. This method fits a parabolic response curve to the data for each species and uses this to estimate species optima; this is distinct from WA, which assumes that this can be approximated by using a weighted average. No previous testate amoebae studies have investigated the contribution that ML models may make. ML models are the most sophisticated of those commonly investigated for palaeoecology, however they have often been outperformed by WA and WA-PLS models in previous studies (Birks et al. 1990).

To assess the relative performance of these three models, two measures are used. The root mean square error of prediction (RMSEP), which assesses the random differences between observed and predicted values, and the maximum bias, which assesses the maximum error in any section of the environmental gradient. Errors are
routinely under-estimated if the training set used for prediction includes those samples, which are used to assess the errors in this prediction. Therefore a cross-validation method needs to be used; the simplest of these is jack-knifing (leave-one-out cross-validation). This method removes one sample at a time from the training set and uses the remaining data-set to derive a model which is then applied to the excluded sample, predicted results can be compared to the measured values (Birks 1995). This method is widely used in testate amoebae transfer function studies, however it has the limitation that the number of iterations is limited by the total number of samples. An alternative method is bootstrapping, this method selects a random set of samples of equal size to the original data-set with each sample able to be selected more than once, a model based on this new data-set is then applied to the remaining unselected samples which form a test-set. As each sample can be selected more than once the number of iterations is unlimited, 1000 cycles were used in this study. RMSEP and Maximum bias estimated by both of these methods are considered in this study (denoted RMSEP\textsubscript{jack}, RMSEP\textsubscript{boot}, Max Bias\textsubscript{jack} and Max Bias\textsubscript{boot}). However for the data-filtering exercise RMSEP\textsubscript{jack} has been used as the primary criterion to allow easier comparison with the results of previous studies. All species-environment modeling was carried out using the program C2 ver. 1.3 (Juggins 2003).

Previous studies have improved the performance of their transfer functions by selectively removing species and samples; here I investigate the effect that this data filtering has and use these methods to optimize model performance. One common data treatment used in several studies is the exclusion of species that occur in only a small number of samples. It follows that the model will be inadequately able to characterize the optima and tolerances of species which only occur a few times and that model performance may be improved by eliminating them. This has been regularly applied in testate amoebae studies, however the precise cut-off point has varied considerably between authors; from species with a single occurrence through species with as many as three (Booth 2001), four (Booth 2002) and even six occurrences (Charman & Warner 1997). In this study I investigate the effect that increasing this cut-off point makes to model performance and the number of species remaining in the data set.
Another commonly used method to improve model performance is by removing those samples which have a high residual, possibly due to unusual testate amoebae communities or inaccurate environmental measurements. Woodland *et al.* (1998) and Wilmshurst *et al.* (2003) have used this strategy in testate amoebae studies. In these studies a single cut-off point was assigned and removing samples with high residuals was shown to improve model performance. Here, I assign a series of cut-off points to see how increasingly stringent filtering effects model performance relative to the number of samples included. Initially this was achieved simply by applying a series of cut-off points to residuals produced using the entire data set. However it was found that model performance could be further improved by using these same cut-off points, but applying them to residuals produced for each successively filtered data set. This iterative methodology produces a small but meaningful improvement in model performance for both pH and DWT reflecting the impact that removing each sample has upon the residuals of the others. A further possible method, which may be used to improve model performance, is by removing those species which have the broadest tolerances and which are therefore less useful as bioindicators. In this study this was investigated using species standard errors by setting a series of cut-off points and using a similar iterative method to the filtering for high residuals.

**2.4 RESULTS**

A total of 21,66 individual amoebae and 18 *Habrotrochoa angusticollis* were counted in 115 samples from the 9 sites. The average total count was 188 per sample (SD 68). A total of 62 species were found and the average species richness per sample was 14.3 (SD 3.8). The five most abundant species in decreasing order of abundance were *Assulina muscorum, Amphitrema flavum, Hyalosphenia papilio, Phryganella acropodia* and *Euglypha ciliata*, these five species accounted for 51.4% of the total. Depth to water table (DWT) was highly variable between sites and samples, ranging from 93cm to 5cm and averaging 35.7cm (SD 18.9cm). The driest site was Moose Pass (average 55.9cm) and the wettest was Kachemak (average 18.3cm). Peat pH varied from 3.8 to 5.8 and
averaged 4.6 (SD 0.4). The most acidic site was Clam Gulch (average 4.4) and the least acidic was Kachemak (average 5.5).

**General data structure & species-environment relationships**

The results of the DCA indicate a relationship to surface wetness, species known to be associated with wet habitats have lower scores on the first axis and species associated with drier habitats have higher scores. The DCA also shows clear separation of samples by sites, a finding that was confirmed by Mantel tests. In the RDA, the site variables and the two quantitative variables (pH and DWT) respectively explained 31.2 and 12.9% of the variation in the species data. Both sets of variables were significant (Monte Carlo permutation test, 999 permutations, $P<0.001$). The partial RDA revealed that 7.1% of the variation was explained by both sets of variables. Therefore the fraction of the variance explained by the site variables only was 24.1% (31.2-7.1%) while the fraction explained by the two quantitative variables (pH and DWT) only was 5.8% (12.9-7.1%). Finally 63% of the variation was left unexplained.

**Species-environment models**

The performance of WA, WA-PLS and ML models was initially assessed using all data except for species occurring in only a single sample, results are shown in Table 1. Several variants of the WA model were trialed, the best performing was simple weighted averaging with inverse deshrinking. The best performing model overall, in terms of RMSEP jack is a two-component WA-PLS model with a value of 15.8cm for DWT and 0.3 for pH (Table 2.1, Fig. 2.2). Errors assessed using bootstrapping are generally greater than those using jack-knifing, consistent with the results of other studies. It is notable that while the ML model performs poorly in terms of RMSEP, it performs best for maximum bias (Table 2.1). Model performance may be improved by selective exclusion of the data; the first method we attempted was by removing those samples with only a small number of occurrences. Results are shown in Fig.2.3a&d, removing species with low occurrences clearly reduces RMSEP jack particularly at higher levels where large numbers of species
Fig. 2.2 Measured vs model predicted values pre- and post-filtering for DWT (a&b) and pH (c&d)
are removed. Removing species occurring in as many as seven samples reduces the total number of species by around a third. However, the decrease in RMSEP_{jack} is not uniform, so for instance removing species with three occurrences from the DWT data produces a greater RMSEP_{jack} than removing species with only two occurrences. To decide what degree of filtering is to be used a balance needs to be reached between model performance and the number of species remaining and therefore the applicability of the model to palaeo-testate communities. In this study it was decided that an optimum filtering would be removing species with two occurrences from the DWT data set and a single occurrence from the pH data set. These filtered data sets were used for the subsequent stage of data filtering.

**Table 2.1** Comparative model performance for full data-set assessed using RMSEP and Maximum Bias values produced by both boot-strapping and jack-knifing.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Model</th>
<th>RMSEP_{jack}</th>
<th>RMSEP_{boot}</th>
<th>Max Bias_{jack}</th>
<th>Max Bias_{boot}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWT</td>
<td>WA</td>
<td>15.9</td>
<td>16.4</td>
<td>44.5</td>
<td>44.7</td>
</tr>
<tr>
<td>DWT</td>
<td>WA-PLS</td>
<td>15.8</td>
<td>16.6</td>
<td>43.3</td>
<td>43.2</td>
</tr>
<tr>
<td>DWT</td>
<td>ML</td>
<td>24.5</td>
<td>21.8</td>
<td>26.7</td>
<td>31.2</td>
</tr>
<tr>
<td>pH</td>
<td>WA</td>
<td>0.30</td>
<td>0.31</td>
<td>0.60</td>
<td>0.65</td>
</tr>
<tr>
<td>pH</td>
<td>WA-PLS</td>
<td>0.30</td>
<td>0.33</td>
<td>0.56</td>
<td>0.66</td>
</tr>
<tr>
<td>pH</td>
<td>ML</td>
<td>0.40</td>
<td>0.40</td>
<td>0.49</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The second method of data-filtering tested was removing samples with high residuals. Results show that this does significantly improve model performance (Fig.2.3b&e). For DWT, removing samples with a residual greater than 10 reduces the RMSEP_{jack} to 7.41 cm, a decrease of over 50%. The samples removed are generally located at the ends of the environmental gradients, particularly from the very dry sites for DWT. Therefore, removing these samples from the data set restricts the environmental gradient for which the transfer function has predictive power when applied to palaeoecological data, a balance needs to be achieved between this and model performance. It was decided that an optimum compromise would be to use the DWT data set with residuals greater than 20 excluded and the pH data-set with residuals over 0.4
Fig. 2.3 Results of data filtering exercise showing change in RMSEP (solid line) and remaining samples or species (dashed line). Filtering for low species occurrences (a&d), high sample residuals (b&e) and high species standard errors (c&f).
excluded, these data sets retain 91 and 103 samples respectively. This cut-off point is approximately 20% of the environmental gradient for both pH and DWT. The final possible method for improving model performance is by removing those species with high standard errors, results of these trials are shown in Fig.2.3c&f. Moderate filtering does slightly reduce RMSEP\_jack for DWT although it makes little difference for pH, however at higher levels RMSEP\_jack is significantly increased. Species initially removed are those with few observations such as *C. platystoma* and *T. dentata*. Under more rigorous filtration more common species such as *T. arcula* and *C. oviformis* are also removed. It was decided not to use this filtering for either DWT or pH as even at low filtering where RMSEP may be decreased slightly, maximum bias is increased. Given the selected data filtering RMSEP\_jack is reduced to 9.7 cm for DWT and 0.21 for pH.

<p>| Table 2.2 Model performance pre- and post-filtering using optimal 2-component WA-PLS model for DWT and pH. |
|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|</p>
<table>
<thead>
<tr>
<th>Model</th>
<th>DWT (full data)</th>
<th>DWT (filtered data)</th>
<th>pH (full data)</th>
<th>pH (filtered data)</th>
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<td>RMSEP_jack</td>
<td>15.8</td>
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<td>0.30</td>
<td>0.21</td>
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<td>Max Bias_boot</td>
<td>43.2</td>
<td>14.2</td>
<td>0.66</td>
<td>0.20</td>
</tr>
</tbody>
</table>

2.5 DISCUSSION

The species coefficients produced by this study show reasonable similarity with the results of other quantitative and qualitative studies of testate amoebae ecology. At the wettest end of the DWT gradient are species such as *Heleopera sphagni* and *Placocista spinosa* and at the driest are species such as *Trigonopyxis arcula*, *Nebela militaris* and *Bulinularia indica*. These results are in keeping with the recognized moisture preferences of these species. It is difficult to compare species optima with previous results as most studies have only measured DWT on a single sampling occasion and therefore do not take account of annual variations in water table. One approach to this is to compare the relative position of species optima on the overall DWT gradient for each study. The plot in Fig. 2.4 compares these results to those of six previous studies; there is good overall agreement. The optima for any given species in this study are generally towards the
Fig. 2.4 Species DWT optima for selected major species expressed as a percentage of measured environmental gradients compared between this study and six others.
middle of the range of optima for that species across the seven studies. Therefore, overall, the ecological patterns of testate amoebae in South-Central Alaska generally compare well with observations from previous studies in other parts of the world. This provides further support for their use as bioindicators over broad geographical ranges.

The proportion of total variance explained by depth to water table and pH was lower in this data than in comparable studies. In this study 5.8% of the variation was explained by the measured environmental variables, other studies have found values of 9.1% (Charman 1997), 9.7% (Booth 2001) and 11.7% (Booth 2002). The proportion of variance explained by the sites (24.1%) was much higher than that explained by pH and DWT (5.8%). This would suggest that the sites differed significantly with respect to some important variable to which testate amoebae are sensitive. Given the relatively large area covered by this study and the important climatic differences among the sites, ranging from sub-oceanic to sub-continental, it is likely that inter-site differences in the extremes or the range of temperature, moisture or other variables may have a strong influence on testate amoebae community structure. Recording such patterns was however beyond the scope of this study and no meteorological data were available.

Model performances have been substantially improved by selective filtering of the data but this improvement is not uniform. To understand the data structure and the impacts of data-removal a step-wise approach is preferable to a single cut-off point as used in previous studies. The methodology used in this study may therefore be useful for improving model performance in other studies. After the selected data-filtering the RMSEP _jack_ for the transfer function is reduced to 9.73 cm for DWT (Table 2.2). This is a considerable improvement upon the full data-set but still compares poorly to the results of other studies which have produced values for RMSEP _jack_ as low as 3.93 cm (Woodland _et al._ 1998), 6.3 cm (Charman & Warner, 1997) and 7.5 cm (Booth, 2001, 2002; Wilmshurst _et al._ 2003). When applied to palaeoecological data this standard of model performance will allow differentiation of wet from dry phases of peat growth but might not detect more subtle surface moisture changes.

A possible cause of this poor performance is a taxonomic bias due to the fact that the analyses were divided among three individuals. To minimize this possible bias a conservative taxonomic approach was used. Significant differences were nevertheless
Fig. 2.5 DWT range against RMSEP for seven previous studies and this study pre- and post-filtering
found among the three sets of data that were pooled in this study, but these differences also reflect true differences among the sites. For example in Bicentennial Bog a wide range of microhabitats were sampled, but overall this is where many of the wetter microhabitats occurred. Jigsaw Lake was the only site adjacent to a true lake, as opposed to small pools in the center of peatlands. The sites also differ in terms of vegetation, which may also affect testate amoebae communities.

Perhaps a more ecologically meaningful explanation for the poor model performance is the unusually dry conditions that characterize many peatlands in South-Central Alaska. In most previous studies the maximum depth to water table recorded ranges between 30 and 50cm (Booth 2001, 2002, Bobrov et al. 1999, Charman & Warner, 1997, Wilmshurst et al. 2003). In this study DWT values as high as 93cm were encountered. In these driest conditions model fit is poorest and it is these samples that are preferentially removed when filtering for samples with high residuals. Poor model fit at the driest sites has been observed in several previous studies (Booth 2002, Lamentowicz and Mitchell in press, Mitchell et al. 1999). It is therefore possible that the presence of some extremely dry sites may have impacted upon model performance. A plot of DWT gradient against model performance for several studies shows a generally good relationship (Fig. 2.5). When assessed by this criterion, model performance in this study seems more reasonable. Fig. 2.5 also suggests a good relationship between the restriction in environmental gradient and improvement in RMSEP jack with data-filtering; the improvement in model performance may therefore have been primarily achieved at the expense of the environmental gradient considered. A balance needs to be reached between model performance and model applicability; this decision remains an essentially subjective one.

A further possible cause of poor model performance is that current and recent climatic change may be causing the study sites to change. During sampling, many of the peatlands on the Kenai lowlands were noted to be severely desiccated with many plants appearing drought-affected. Much research has illustrated recent climatic change in the Arctic and sub-Arctic regions (Moritz et al. 2002, Sturm et al. 2001). In south-central Alaska, Klein et al. (submitted) have suggested a variety of evidence for wetland drying caused by climatic change over the last 50 years. If the climate of the region, and
therefore the hydrology of the peatlands, is in a state of transition then it is possible that the testate amoebae community may not have fully adjusted to the change, especially since the sampled depth (3-5cm) integrates conditions over several years. This might depend on the location, hydrology and climate of the individual peatlands and could have decreased the model fit.

This study provides the first testate amoebae transfer function for southern Alaska and indeed the entire North Pacific region. This work allows quantitative interpretation of testate amoebae community changes in terms of pH and DWT. Results demonstrate that the ecological preferences of testate amoebae species are broadly similar to other regions of the world. Overall model performance is somewhat below that of previous studies, this may be due to a combination of recent climatic change and the large environmental ranges in this study.

In terms of the palaeoecological investigations in this thesis, the transfer function will allow quantified reconstruction of DWT and pH changes across the tephra layers with associated error estimates. This may allow it to be determined if any impacts are occurring and to deduce whether these are caused by changes in pH or DWT.

**Key Findings**

- The distribution of testate amoebae in south central Alaskan peatlands is controlled by DWT and pH. The transfer function allows quantitative reconstruction of these properties from palaeoecological records.
- The ecology of testate amoebae species in Alaska is similar to other regions of the world.
- A step-wise approach to data-filtering may be valuable for improving model performance in transfer function studies.
CHAPTER 3. ECOLOGICAL EXPERIMENT

3.1 INTRODUCTION

As has been discussed previously, one of the key themes in this research is to investigate volcanic impacts on peatlands and to separate direct from indirect processes. Little ecological research has addressed the issue of direct volcanic impacts on peatlands, there is therefore a very poor understanding of the potential mechanisms by which volcanoes may impact upon peatlands. The literature review has highlighted several possible changes to peatland functioning that might be caused by the deposition of volcanic products. However there is a good deal of uncertainty regarding the possibility of these impacts and their magnitude. To enable interpretation of the palaeoecological record an improved understanding of the potential processes occurring is required. This therefore calls for neo-ecological research. Direct observation of volcanic impacts is difficult due to the unpredictability of eruptions; the most practical approach is therefore experimentation. A previous experimental study has been carried out by Hotes et al. (2004). However this study was carried out on sites different from those in this study, did not consider those variables most relevant to the palaeoecological record and had various problems in it's formulation, it is therefore of limited usefulness for interpreting the results of this study.

To address these issues, an experimental approach is used here (the experiment is also described by Payne & Blackford in press a). This experiment is focused on how impacts upon peatlands may be represented in the palaeoecological record. The main means of monitoring impacts on the site are therefore the same attributes that are used in the palaeoecological studies- peat humification, testate amoebae and plant community composition. An experimental approach requires repeated site visits; it was therefore unfeasible to use a site in Alaska for the experiment. The site used was in western Scotland; this site is different from the sites in Alaska but does have some key features in common. The study was primarily focused upon the affects of volcanic acidity as this was not addressed by Hotes et al. (2004), a secondary consideration is the physical impacts of tephra.
A particular focus of this experiment is the effects of the Hekla-4 eruption. Tephra from this event has been found in numerous peatland sites from Britain and Ireland (Dugmore et al. 1995, Pilcher et al. 1995), the Faeroe Islands (Edwards et al. 1994), and continental northwest Europe (van den Bogaard & Schmincke 2002, Persson 1971). It is this eruption that has been at the center of much of the recent debate over volcanic impacts in the British Isles (Blackford et al. 1992, Grattan & Gilbertson 1994, Edwards et al. 1994, 1996, Birks 1994, Charman et al. 1995, Dwyer & Mitchell 1997, Caseldine et al. 1998, Grattan et al. 1998, 1999, Hall 2003). Results from this experiment may therefore add to the continuing debate.

3.2 SITE

The site used in this experiment is the Moss of Achnacree in Argyll and Bute, western Scotland (Grid Reference NM9134; Fig 3.1). The site is a large raised bog covering an outwash plain on the north shore of Loch Etive as it enters the Forth of Lorn (Gray 1993, Whittington 1983). Peat deposits cover an area of almost 7Km$^2$ averaging around 1.9m depth. The site receives an annual rainfall of around 1500mm (Scottish Environmental Protection Authority, unpublished data). The area has been occupied by humans since at least the Bronze Age and the bog has been disturbed by grazing, drainage and peat cutting, particularly in recent centuries (Whittington 1983, Scottish Natural Heritage & Scottish Wildlife Trust unpublished data). Due to this anthropogenic disturbance the site contains a complex mosaic of vegetation types. Away from the margins, the dominant species are Calluna vulgaris and Eriophorum vaginatum with Pleurozium schreberi, Hypnum cupressiforme, Cladonia portentosa and Sphagnum capillifolium. In areas that have been cut and have inhibited drainage Sphagnum magellanicum and Sphagnum papillosum are more common. In areas disturbed by grazing Molinia caerulea and Deschampsia flexuosa have increased abundance (Scottish Natural Heritage & Scottish Wildlife Trust unpublished data).

This site fulfills several of the major requirements for this study. The site contains a variety of species common in the peatlands of northern Europe; results will therefore have wider relevance. The site receives little contemporary acidity due to anthropogenic
Fig. 3.1 Location of Moss of Achnacree site and experimental plots
acid rain and should be in a fairly natural acidity state (Scottish Environmental Protection Authority 2001, Skiba et al. 1989). In addition, the tephrochronological record indicates that this region may well have received tephra deposition in the late Holocene, increasing the relevancy of this study to the palaeoecological record (Dugmore et al. 1995).

This site clearly has some differences from those used in the palaeoecological studies, however it also has several common features. The site is a raised bog and is therefore similar in morphology to many of the ombrotrophic sites in Alaska. Western Scotland has a broadly similar mild and oceanic climate to southern Alaska. 1500mm annual rainfall at the Moss of Achnacree compares to 1300mm at Juneau, AK although Alaskan winters are colder, January average temperature of 5°C in Oban compares to −3°C in Juneau. The vegetation of the site also bears some similarity, several species found on this site were also found on peatlands in Alaska (e.g. Aulacomnium palustre, Cladonia portentosa) and where the same species were not found others of the same genus often were (e.g. Eriophorum, Hypnum). The Scottish site has abundant Calluna vulgaris; this species is not present on the Alaskan sites however Empetrum nigrum does fill a similar niche in some locations. The majority of the testate amoebae species found at this site were also found in Alaska. It is therefore hoped that findings from this site will be broadly applicable to the palaeoecological studies.

3.3 METHODS

To investigate the impact of volcanic fall-out at increasing distances from the eruptive source, a variety of different quantities of tephra and associated acids were applied to a series of plots on the site. The minimum value used was 1gm⁻² of tephra, as indicated by concentrations of Hekla-4 tephra found in northern Ireland (1TKm⁻²; Pilcher et al. 1994). The maximum value used was 700gm⁻² as indicated by the highest concentrations found in Caithness, northern Scotland (0.16g per 2.2cm² sample; Dugmore & Newton 1992, A.Dugmore pers. comm.). Intermediate values of 50 and 200 gm⁻² were also used to give a range of treatments.

Tephra to be applied to the plots was obtained from a series of exposures near Kirkjubæjarklaustur in southern Iceland. The deposits are thought to be from the AD1362
eruption of Öraefajökull (Ellershaw 2004, Thórarinsson 1958, Larsen et al. 1999). It is thought unlikely that the slight differences in major element composition between this tephra and Hekla-4 would make any difference to this study. The tephra deposits were thoroughly washed in distilled water to remove external contaminants and sieved at 150µm to approximately simulate the size of northern British tephra deposits. To investigate the possibility that the impact of tephra may be particle-size dependent, two plots had larger tephra (150-300µm) applied.

As well as investigating the effects of tephra particles alone, simulations of acid loading were also attempted. In the interests of experimental feasibility and given the uncertainties involved in assessing the composition of volcanic emissions from ancient eruptions, it is necessary to make several assumptions about the composition of volcanic acid precipitation from Hekla-4 based on the available literature.

1. Firstly, that the volume of volcanic acid precipitation is directly proportional to the amount of tephra deposited. Volcanic acids are deposited through a variety of mechanisms including directly through volcanic aerosols and adhering to tephra particles. Modern studies show that volcanic acid precipitation varies on a fine scale (Armienta et al. 2002); for ancient eruptions there is no way to fully understand the spatial dimensions of this precipitation as no direct record is left in sediments. However, tephra is preserved in sediments and this allows the potential to reconstruct at least that component of acidity which adheres to tephra. In this experiment I assume that the quantity of acid deposited is directly proportional to the quantity of tephra deposited at a site. In addition it is assumed that the quantity of tephra recovered from a peat core is an accurate indication of the quantity deposited at a site.

2. Secondly, that for the Hekla-4 eruption we can assume a 1:1 ratio of tephra to acid. Oskarsson (1980) looking at products from the Hekla-1970 eruption noted that at distance from source, the mass of adsorbed volatiles approached that of the tephra itself. In their theoretical assessment of the possible impacts of Hekla-4 in northern Britain, Grattan & Gilbertson (1994) followed this, assuming a 1:1 relationship between tephra and adsorbed acids. Although this is probably a considerable simplification, it remains the best approximation we can make based on very limited
evidence. In this study this scenario is tested by using the same mass of approximately 1M acid and tephra for each experimental plot.

3. Finally, that all ecological impacts from volcanic precipitation are due to sulphuric acid. Volcanic precipitation is a complex and highly variable mixture of compounds, dominated by sulphuric acid but also including several other acids (particularly HCl and HF) and other compounds. Modern studies of acid precipitation impacts show the great potential of sulphuric acid to impact upon peatland vegetation (Smith et al. 1993, Ferguson et al. 1978). It therefore seems reasonable to assume that most impacts from volcanic acid precipitation are due to sulphuric acid, this acid alone was used in the majority of experiments. However, to investigate the possibility of differential impacts from other acids, one plot had only HCl applied and another a approximately 2:1 mixture of H₂SO₄ and HCl, the approximate ratio found by Devine et al. (1984) from melt-inclusions of Hekla-3 tephra.

In addition to the treated plots, two control plots with only distilled water applied were also used. To separate the impacts of acid and tephra, several plots with either acid or tephra were also used. To account for local factors, two of the experiments were duplicated in different areas of the site. Full details of each treatment are shown in Table 3.1.

A series of fourteen plots were placed on the site at a location approximately 100m from the western margin of the mire (Fig.3.1). Plots were each 1m² and were marked by metal pegs. Plots covered various microforms and vegetation types on the bog surface. Tephra and acids were applied to the plots in May 2002. Tephra was applied to each of the plots in suspension in the acid (or water) using a domestic watering can, with the exception of the coarser tephra which was sprinkled on by hand. Care was taken to ensure an even application across each plot. Each volume of acid was made up to 11 with distilled water before application. The apparatus was washed out with a further 31 of distilled water after each application and treatments were followed by rainfall within 12 hours. Plywood sheets were placed around the plots during application to ensure that all tephra and acid remained within the treated area. Plots were visited again in June 2002 (1
month), September 2002 (4 months), November 2002 (6 months), May 2003 (12 months), September 2003 (16 months) and May 2004 (24 months).

Table 3.1 Treatment of experimental plots

<table>
<thead>
<tr>
<th>No.</th>
<th>Vegetation &amp; Microform</th>
<th>Treatment</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calluna dominated low hummock with Cladonia portentosa</td>
<td>Distilled water only</td>
<td>Control</td>
</tr>
<tr>
<td>2</td>
<td>Calluna and Eriophorum dominated low hummock</td>
<td>Distilled water only</td>
<td>Control</td>
</tr>
<tr>
<td>3</td>
<td>Hollow and hummock-edge, Calluna and Sphagnum</td>
<td>700g Tephra (sieved at 150μm) &amp; 700ml H₂SO₄</td>
<td>Maximum quantities</td>
</tr>
<tr>
<td>4</td>
<td>High hummock, Calluna with Cladonia portentosa and Eriophorum</td>
<td>1g Tephra (sieved at 150μm) &amp; 1ml H₂SO₄</td>
<td>Minimum quantities</td>
</tr>
<tr>
<td>5</td>
<td>High hummock, Calluna dominated</td>
<td>50g Tephra (sieved at 150μm) &amp; 50ml H₂SO₄</td>
<td>Intermediate quantities</td>
</tr>
<tr>
<td>6</td>
<td>High hummock, Calluna dominated</td>
<td>1g Tephra (sieved at 150μm) &amp; 1ml H₂SO₄</td>
<td>Duplicate of 4</td>
</tr>
<tr>
<td>8</td>
<td>Hummock-edge, Calluna and Cladonia portentosa dominated</td>
<td>200g Tephra (sieved at 300μm) &amp; 200ml H₂SO₄</td>
<td>Tephra size experiment</td>
</tr>
<tr>
<td>9</td>
<td>Low hummock, Calluna and Eriophorum dominated</td>
<td>50g Tephra (sieved at 150μm)</td>
<td>Tephra impact without acid</td>
</tr>
<tr>
<td>11</td>
<td>Hummock-edge, Calluna dominated</td>
<td>700ml H₂SO₄</td>
<td>Acid impact without tephra 1.</td>
</tr>
<tr>
<td>12</td>
<td>High hummock, Calluna dominated</td>
<td>700ml H₂SO₄</td>
<td>Duplicate of 11</td>
</tr>
<tr>
<td>13</td>
<td>Hummock-edge, Calluna and Cladonia portentosa dominated</td>
<td>450ml H₂SO₄ + 250ml HCl</td>
<td>Acid composition experiment 1.</td>
</tr>
<tr>
<td>14</td>
<td>High hummock, Calluna dominated</td>
<td>700ml HCl</td>
<td>Acid composition experiment 2.</td>
</tr>
<tr>
<td>15</td>
<td>Low hummock, Calluna and Hypnum cupressiforme</td>
<td>50g Tephra (sieved at 300μm) &amp; 50ml H₂SO₄</td>
<td>Tephra size experiment 2.</td>
</tr>
</tbody>
</table>

Before application and at six intervals over the subsequent 24 months, vegetation was surveyed and photographed and soil samples taken. Peat samples were taken using a 5cm bore Russian-pattern peat corer from the uppermost 25cm of peat. Sample locations within the plots were selected at random using a random number and grid system. To
exclude marginal effects no samples were taken within 10cm of the edge of the plots.

Peat samples were returned to the lab and refrigerated until analyzed.

At each sampling, vegetation was described and species cover estimated on the DOMIN scale (Rodwell 1991). Unfortunately the errors in these estimations are generally too great to allow any changes to be accurately assessed. Digital photographs were taken at the time of each sampling. To assess any possible impact on flowering, the September 2002 photograph was further analyzed. A 10x10 grid was superimposed onto the image, the number of squares of this grid in which any flowering of Calluna vulgaris was observed were then counted. This figure was divided by the abundance of C. vulgaris estimated in the field to provide an estimate of overall flowering.

A sub-set of five plots (plots 1,3,5,8 and 11) was selected for further study of peat properties and variables relevant to the palaeoecological record. These plots represent a cross-section of the acid treatments from no acid applied to maximum quantities. Attributes investigated include humification and testate amoebae, key palaeoecological proxies and pH. pH was measured from the surface of each peat sample. For the purpose of this study, the surface was taken to be the base of the green, photosynthesizing layer, for the drier sites this is effectively the upper surface, for moss covered sites this may be a centimeter or more below the surface. A known volume of peat (approximately 1cm³) was disaggregated in 50ml of distilled water and pH measured using a Hanna Instruments 8424 pH-meter after one hour. Samples for testate amoebae analysis were prepared following the method of Hendon & Charman (1997) as used for the palaeoecological analyses, full details of this method and the preparation are discussed in section 5.5. A count of 100 tests was used in this experiment, the taxonomic scheme adopted is that of Charman et al. (2000) to ensure maximum comparability with the transfer function used, this scheme is not identical to that used in the palaeoecological studies. Results were plotted as stratigraphic diagrams using C2 v.1.3 (Juggins 2003).

Quantitative interpretation was carried out using transfer functions. The study of Woodland et al. (1998) from many sites across the UK was used as the main transfer function for depth to water table (DWT), the main climatic proxy. This transfer function includes results from a number of similar raised mires from across the UK including one site in western Scotland. Other transfer function studies have included pH, a property that
is also relevant to this research. However, pH has not been measured in any UK study, the nearest study which includes pH is that of Mitchell et al. (1999) from the Swiss Jura mountains. While there are clearly differences between the ecosystem and the testate amoebae communities of those sites and this, many studies have shown that testate amoebae species and environmental preferences are comparable across broad geographic areas (Booth 2001, Finlay et al. 2001). As the majority of testate amoebae species found in this study are also included in the Swiss study it is possible to use that study to interpret the results of this in terms of pH, although with some element of caution. There are differences in the taxonomic scheme adopted in the Swiss and UK transfer functions, therefore to allow analysis of the results of this study the taxonomic scheme has been adjusted to fit the requirements of each transfer function.

Cores were sub-sampled for peat humification analysis using contiguous 1-cm samples through the upper 10cm of the core. Humification was measured using the standard, alkali extraction and colorimetry method of Blackford & Chambers (1993) as for the palaeoecological analyses, this method and the technique in general is discussed in section 5.4.

3.4 RESULTS

3.4.1 Impacts on plants

The impact of acids upon the plant communities of the treated plots was striking. The greatest impacts were seen in plots 3, 11 and 12 in which 700ml of sulphuric acid was applied. In these plots, first effects were seen within 24 hours of the additions with heather (Calluna vulgaris) attaining a 'battered' appearance and some reddening of the leaf tips. Following this within three days, effects were also seen on the moss Hypnum cupressiforme with it attaining a bleached appearance. By a month after the initial application (June 2002), changes were dramatic with the majority of plants appearing dead or dying. The moss flora attained a bleached appearance, especially noticeable in Sphagnum magellanicum. The exceptions to this were a small number of plants in marginal areas of the plots which may have received less acid than those nearer to the center. The only species to show no visible change at this stage was the lichen Cladonia
portentosa. However, it is difficult to visually assess the effects on this species due to the lack of chlorophyll. Four months after applications (September 2002), the impacts of the additions were highly pronounced with most plants clearly dead and in obvious contrast to surrounding untreated areas. This dead appearance continued through the first winter with no signs of any new growth until the following year. When the plots were surveyed again, twelve months after the initial applications (May 2003), there were some limited signs of recovery to these three plots. In plots 11 and 12 new growth of Eriophorum vaginatum was observed, although this was less pronounced in plot 3. In all plots, some marginal C.vulgaris plants appeared to produce significant new growth and in plot 3 a few C.vulgaris seedlings were also noted. However, in all three of these plots no sign of new growth or recovery in the moss flora was observed until September 2003 when some new S.magellanicum was noted in plot 3. From September 2003 several Drosera spp. plants were noted growing among dead S.magellanicum in plot 3, these had increased in abundance by the end of the 24-month study period in May 2004. This species was not found anywhere else within the study area. At the end of the study period impacts upon these three plots remained drastic with the majority of plants dead and the plots remaining in marked contrast to the surrounding areas. New growth was limited to marginal plants, some E.vaginatum and a few C.vulgaris seedlings. With the exception of a small number of S.magellanicum plants in plot 3, there was no new bryophyte growth.

In plots 13 and 14 to which a mixture of acids (plot 13) and HCl alone (plot 14) were applied, effects were less pronounced than above but still significant. In plot 13, while the majority of C.vulgaris was killed (over 90%), several plants, particularly around the edges of the plots showed continuing signs of life and new growth was more rapid than the heavily treated plots. By the end of the study period the vegetation was still notably affected but there was significant new growth of E.vaginatum throughout, some new C.vulgaris and a significant amount of healthy Odontoschisma sphagni although no bryophytes. In plot 14 significantly less C.vulgaris appeared to have been killed; around 60% of plants. Although the vast majority of H.cupressiforme plants in this plot appeared to have been killed, another bryophyte, Aulacomnium palustre was largely unaffected.

In plots 5,8 and 15 in which 50ml (plots 5&15) and 200ml (plot 8) of sulphuric acid were applied, effects were limited. In plot 8, C.vulgaris was noticeably affected,
Fig. 3.2 *Calluna vulgaris* flowering in experimental plots, expressed as a percentage of estimated total abundance
with some initial reddening of leaf tips and later loss of foliage. However, this was on a much lesser scale than in other plots with only around 10% of plants affected. Some *H.cupressiforme* appeared dead although there were no pronounced effects on the other bryophytes present (*Aulocoomnium palustre*, *Sphagnum papillosum* and *Sphagnum magellanicum*). In plots 5 and 15 effects were very slight. While some initial reddening of the tips of *C.vulgaris* was noted, plants were not killed in significant numbers and the plots appeared to be in a similar condition to the control plots and surrounding untreated areas.

In the plots which had only 1ml of acid applied (plots 4&6), the plot in which tephra alone was applied (plot 9) and the control plots (plots 1&2), no significant changes were observed and the vegetation remained in a comparable condition to that in surrounding unaffected areas.

A more objective method of determining plant health is to look at attributes such as flowering, this was undertaken for the most abundant species *C.vulgaris* in September 2002. Results (Fig.3.2) largely corroborate the field observations discussed above. At the highest volumes of acid, flowering was limited and almost exclusively confined to marginal plants. Flowering was also noticeably reduced in plot 8 treated with 200ml of acid. Perhaps the most interesting result is that in the plots treated with 50ml of acid, flowering does appear notably reduced compared to the control plots. This might indicate that plant health was affected by the acid additions despite no observation of plant-kills in the field. There was no evidence for reduced flowering in the plots with only 1ml of acid applied or with tephra alone.

### 3.4.2 Surface pH

Surface sample pH results are shown in Fig.3.3. It can be seen that in all studied plots except plot 5 there is an initial decrease in pH values. This may represent acidification due to the acid additions, although it also occurs in the control plot 1 which may count against this idea. In all the plots there is some indication of an upward trend in pH values although there is a good deal of variability. In all the plots the pH value on
Fig. 3.3 Summary results for five plots showing testate amoebae inferred depth to water table (TI-DWT) and pH (TI-pH), surface pH and averaged humification (% transmission)
<table>
<thead>
<tr>
<th>Plot 1</th>
<th>Plot 3</th>
<th>Plot 5</th>
<th>Plot 8</th>
<th>Plot 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ampylina testata</td>
<td>Ampylina testata</td>
<td>Ampylina testata</td>
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<td>Acutula maculata</td>
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<tr>
<td>Acutula demissum</td>
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<tr>
<td>Cypriella attenuata</td>
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final sampling is either the highest or nearly highest of the entire sequence. This upward trend is most marked in plots 3 and 11 which received the greatest volume of acid. While sub-sampling the cores, a distinct ‘rotten eggs’ smell of hydrogen sulphide was noticed from some cores. This smell was present in several samples from plots with 700ml of sulphuric acid applied and was noted from the third sampling (September 2002) onwards.

3.4.3 Testate amoebae

Results from testate amoebae analysis are shown in Fig.3.4. Few distinct trends can be seen for individual species through the time period, where trends are noted within plots they are not replicated between plots. For instance, in plot 3 *Cyclopyxis arcelloides* type shows a distinctive pattern, reaching a peak on the fourth sampling occasion. However, in plot 11 which had a similar acid treatment and would therefore be expected to respond similarly, *C.arcelloides* type is actually lower than previously at this stage. In the majority of the plots testate amoebae communities pre- and post-treatment are very similar. When these results are interpreted using transfer functions (Fig.3.3) few notable trends can be seen. Indeed, the most consistent trend in any plot is a trend of decreasing inferred depth to water table (TI-DWT) and increasing inferred pH (TI-pH) in plot 1, the control plot. Plots of TI-DWT and TI-pH show a strong negative relationship, plots of TI-pH agree reasonably well with measured pH.

3.4.4 Humification

Fig.3.5 shows humification profiles from the sub-set of five plots for all sampling occasions. Results are shown as percentage transmission at 540nm, higher values represent less humified peat and are taken as representing wetter conditions in the palaeoecological record. The first obvious feature to note is the lack of consistency of results within plots. For instance in plot 5, the humification plot on the fifth sampling occasion is characterized by very high transmission mid-core with lower values at either end. This pattern is seen to a lesser extent on the second sampling occasion and to some extent on the first and third, however on the fourth, sixth and seventh occasion there is no
Fig. 3.5 Humification profiles through the uppermost 10cm of peat expressed as % transmission for five experimental plots
trace of this pattern. There is still less consistency in humification profiles between plots, this mid-core peak is seen in only a minority of plots and the overall pattern varies greatly. There is also little consistency between the transmission values on different sampling occasions. For instance for plot 3, transmission values averaged over the 10cm profile vary between under 40% and over 60% (Fig. 3.3). This variation does not constitute a consistent trend and there is also variation in the control plot, although to a lesser extent. It is perhaps worth comment that the greatest variability in average transmission values is in plots 3 and 11, which are also the most heavily treated plots although this may simply be coincidence.

3.5 DISCUSSION

This experiment shows good evidence that rapid acid deposition similar to that produced by distant volcanic eruptions may have considerable effects on peatland plant communities. At the highest concentrations, these effects are severe and persist for at least two growing seasons. Several studies have shown that following vegetation removal during peat cutting it may take several decades for vegetation to completely recover (Joosten 1995). In this case recovery is likely to be more rapid as adjacent vegetation and a seed bank remain intact. However based on the rate of recovery observed so far it seems probable that it may take at least five years for the vegetation of these plots to recover.

This study also suggests differential sensitivity to acid deposition in the plant species present on this site. Bryophytes were especially affected and there is some evidence that Hypnum cupressiforme was particularly sensitive. There is also evidence that at lower acid concentrations, even when plants are not killed outright, their health is impaired. This is demonstrated by the apparent reduction in flowering of C.vulgaris in plots 5 and 15. This is of particular relevance to palaeoecological studies of past volcanic impacts because it indicates that under these conditions pollen production might be reduced without any corresponding change in plant community composition.

This study provides no evidence for the idea that tephra may have had a direct physical effect on these ecosystems. In this study it appears that all the effects arise
through acidity. No impacts were noted in the plot with solely tephra applied and impacts
are similar between acid treated plots, with and without tephra. The pH results show
apparent increases in surface peat pH through the sampling period. The pH drop in many
of the plots by the second sampling is presumably due to the acid addition although the
pH drop in the control, plot 1, means that this is not certain. This pH reduction is rapidly
replaced by significant although variable increases in pH. Peat bog pH is regulated by
two main mechanisms, the cell-wall polyuronic acids produced by Sphagnum and other
plant species and the complex organic (humic & fulvic) acids contained within the peat
(Clymo 1987, Gorham et al. 1984). The increase in pH values suggests that either one or
both of these mechanisms may be disrupted. This could either be due to the death of
plants as observed in the field or increased leaching of organic acids as suggested by the
results of Sanger et al. (1994). As the humification results showed no trend of decreasing
humification (increasing % transmission), a reduction in polyuronic acid production
seems the more likely explanation. A further possible way by which pH could be
increased is by the leaching of metal cations from tephra, increasing alkalinity. This may
be possible with fresh tephra but it seems unlikely that significant leaching from this
tephra would occur as it has previously been exposed to in-situ leaching for several
hundred years.

The lack of any consistent change in testate amoebae communities is perhaps
surprising. The drastic impacts of high acid concentrations upon the vegetation would
suggest similarly major changes in the below ground environment, which we would
expect to be reflected in changing testate amoebae communities. Peat pH has been shown
to be an important factor in determining testate amoebae communities (Heal 1962,
Mitchell et al. 1999), given the apparent changes in pH noted in this study it is surprising
that no distinct effect is noticed. In addition, the presence of a hydrogen sulphide odour in
some of these samples suggests bacterial reduction of sulphuric acid. This may suggest a
shift in decomposition processes away from methanogenesis as discussed by Gauci et al.
(2002). As some testate amoebae species are bacterivorous (Gilbert et al. 2000) it is
possible that there are also changes in the abundance of the amoeba's food sources that
could also have an impact on species abundances.
There are several factors which may have contributed to the lack of testate amoebae response to the additions. A first possibility is that the length of the study period was insufficient to detect a species response. This seems unlikely given the probable generation time of testate amoebae species. Manipulation experiments have found responses to environmental change in time periods less than this study (Lousier 1974, Schönborn 1992). A complicating factor is that the majority of tests examined were empty by the time of counting. It is therefore difficult to know whether the testate amoebae community counted under the microscope was a true representation of that living on the mire surface or was mostly made up of empty tests accumulated prior to the experiment. Another possible explanation for the lack of a testate amoebae response is that the intra-plot heterogeneity of testate amoebae assemblages is greater than any response. Mitchell et al. (2000a) have demonstrated significant heterogeneity in testate amoebae communities even over a smaller and more homogeneous plot than those in this study. In addition, testate amoebae vegetation preferences have been previously noted (Mitchell et al. 2000b). It therefore seems probable that at least some of the variation in the data is due to variation in testate amoebae communities within the plots. This is almost certainly the case in plot 1, this plot was the control and also one of the most homogenous in vegetation composition. In plot 3 the pre-application sample has a much lower TI-DWT than subsequent samples which could be interpreted as an impact of the applications. However this core came from a marginal location which is much the wettest area of the plot. It therefore seems probable that the variation in testate amoebae communities overall is due in large extent simply to intra-plot variability. While these results provide no support for an impact of acid precipitation upon testate amoebae communities, they cannot discount the possibility.

The humification results do not show any distinct trends in overall values or consistency in pattern. The averaged values fluctuate a great deal within plots, similar to the testate amoebae data this may be due in large part to intra-plot variations. In many plots vegetation and topography is heterogeneous and cores may be from drier or wetter regions and may include different vegetation. This random variation may introduce noise into the humification data. Harder to explain is the lack of consistency in the pattern of humification profiles between and within plots. If this near-surface humification was
primarily a function of climatic change we would expect a good deal of consistency both within and between plots. Possible factors contributing to this are differences in climatic sensitivity between hummock and hollow sites, differences in vegetation type and differences in peat accumulation rates. The literature suggests that direct impacts of acid precipitation upon peat humification might be possible through enhanced leaching of organic acids (Sanger et al. 1994) or enhanced microbial activity. This study provides no indication that such impacts are occurring; however the great variability of results means that they cannot be entirely ruled out.

When interpreting these results consideration needs to be taken for the underlying uncertainties and the assumptions upon which this study is based. This study is also a single set of experiments on a single site over a single time period, it is possible that under different conditions the response might be different. However, this study does provide a test of the potential impacts of one scenario, which has been previously suggested as reasonable (Grattan & Gilbertson 1994). The results show that impacts upon vegetation may be significant while any impacts upon other variables are more equivocal. However, it does provide a basis on which future studies can develop.

It is not possible to directly apply these results to the case of Hekla-4 impacts in northern Britain due to the uncertainties regarding the underlying assumptions. However the results do provide some support for the suggestions of Grattan & Gilbertson (1994) that vegetation impacts could have been due to volcanic acids. It is interesting to note that no impacts were present at the lowest application (1ml per plot) designed to approximate tephra deposition in northern Ireland while impacts of the highest application designed to simulate deposition in northeast Scotland (700ml per plot) were drastic. This provides some support for the idea that the difference in impacts between studies in Scotland (Blackford et al 1992, Edwards et al. 1994) and Ireland (Hall et al. 1994, Hall 2003, Caseldine et al. 1998) could have been due to differences in acid deposition. Grattan & Gilbertson (1994) attempted to assess the impacts of volcanic acid deposition by reference to critical load values for the peatlands. It is interesting to note that even the lowest acid application in this study exceeded the annual critical load value for this site (and indeed for the sites in northern Ireland). This may suggest that critical loads are a poor criterion for determining impacts following a single acid deposition event.
In terms of the palaeoecological studies, this experiment suggests several potential features of a volcanic acid deposition event that may be detectable. The results show severe acid impacts on plants which could be represented in the palaeoecological record as a peak in UOM as the plant material is degraded. Results show that bryophytes might be particularly sensitive to acid deposition suggesting Sphagnum could be reduced in the macrofossil record. If plant growth is substantially reduced, a reduction in peat accumulation rate is possible. Results do not show evidence of impacts on testate amoebae or humification. However it seems probable that testate amoebae at least would be affected by the acid impacts on these sites given time- species would be expected to respond to impacts on plants, a change in pH or a change in bacterial communities.

**Key Findings**

- There is at least the possibility for volcanic acids to severely impact on peatland plants.
- There is no evidence for volcanic acids and tephra to directly affect humification and testate amoebae but this may be due to experimental limitations.
- There is no evidence for an impact of tephra alone on any of the variables considered.
- Volcanic acids provide a possible mechanism by which tephra deposition could have affected the vegetation of northern Britain and Ireland.
CHAPTER 4. TEPHRA TAPHONOMY EXPERIMENT

4.1 INTRODUCTION

The main aim of the palaeoecological work in this thesis is to relate changes in the palaeoecological record to a tephra layer to investigate any volcanic impacts. This linkage between the palaeoecological record and the tephra layer may be imperilled if tephra undergoes significant post-depositional movement. An experiment was therefore carried out to investigate the extent of tephra movement and factors that may contribute to this. This experiment is also described by Payne et al. (submitted b).

That tephra does not move substantially through the sedimentary column is a fundamental assumption of peatland tephrochronology, however it is an assumption that has attracted minimal research. Lake sediment studies have observed significant movement of tephra with secondary deposition, biological mixing processes and density-related movement with redeposition at lower levels (Anderson et al. 1985, Thompson et al. 1986, Boygle 1999, Beierle & Bond 2002). These problems can impair correlations and dating based on tephras. In peat there is also evidence that depositional processes are not as straightforward as is often assumed. Bjarnasson (1991) noted the sinking of Icelandic tephra through a moss carpet. Tephra may be redeposited due to wind action and problems may be exacerbated if the peat surface is frozen (Bergman et al. 2004). In the sedimentary record, some tephra profiles have been noted to have secondary and subsidiary peaks (e.g. Caseldine et al. 1998) and some sites appear to have a background tephra concentration, which might be due to tephra movement through the peat (Charman et al. 1995, Holmes et al. 1999).

Dugmore & Newton (1992) used X-radiography to examine the horizontal variability of a micro-tephra layer in peat. Their study showed an uneven distribution across the palaeo-bog surface with greater quantities found in downward projecting pockets, presumably representing tephra washing into hollows. Caseldine et al. (1999) have also shown fine-scale horizontal variability in tephra concentration by examining the reflectance properties of tephra layers in peat. These studies suggest that an improved knowledge of tephra taphonomy is essential to the continued use of tephrochronology. Both vertical and horizontal movement of tephra are potentially significant. If tephra moves vertically through the peat profile this could result in an
erroneous age being assigned to the sediment. Horizontal movement of tephra could potentially result in concentrations being reduced below detection limits and a valuable isochrone being lost.

One possible means of investigating tephra taphonomy is to use an experimental approach. Rowley & Rowley (1956) and Clymo & Mackay (1987) investigated the taphonomy of pollen in peat using experimental approaches and illustrated substantial movement. These studies cannot be directly applied to tephra due to the differences in tephra morphology and size range, however similar methodologies may be applied to a study of tephra taphonomy. This may have additional relevance due to the suggestion of Hall & Pilcher (2002) that tephra concentration profiles may provide a guide to the taphonomy of pollen and other microfossils. In this experiment a series of field experiments was used to investigate the taphonomy of tephra in peat. Experiments were designed to investigate changes in the horizontal and vertical distribution of tephra through peat over time, both macro and microscopically.

4.2 MATERIAL & METHODS

This study was carried out in conjunction with the ecological experiment described in Chapter 3, the Moss of Achnacree site has already been described in that chapter. Results from three plots are reported here: Plot 15 (50g tephra per m²), Plot 9 (50g tephra per m²) and Plot 21 (300g tephra per m²). Full details of applications and sampling are shown in Table 4.1. Plots 15 and 9 are hummock sites and have similar vegetation, dominated by *Calluna vulgaris* and *Eriophorum vaginatum* with an understorey of *Cladonia portentosa*, *Hypnum cupressiforme*, *Aulacomnium palustre* and *Odontoschisma sphagni*. The surface peat in these plots is relatively compact and well humified. Plot 21 is a hollow site and has a *Sphagnum*–dominated vegetation community including *Sphagnum magellanicum*, *Sphagnum recurvum*, *Eriophorum vaginatum* and *Odontoschisma sphagni*. The surface peat in this plot has a much looser structure.
Tephra applied to the plots was the same Öraefajökull tephra and the method of application was as described in the previous chapter. Tephra applied to Plots 9 and 21 passed through a 150µm sieve while that applied to Plot 15 was in the size range 150-300µm. Tephra was applied to Plots 9 and 15 in May 2002. To investigate tephra movement down through the peat column with time, cores taken from Plot 15 at five intervals over the two-year study period (1, 4, 6, 13 and 24 months) were examined for tephra. In June 2003 tephra was applied to Plot 21, after three days a monolith block (10x10x20cm) was extracted from the centre of this plot and another from Plot 9. These blocks were used for the preparation of thin-sections to examine the micro-distribution of tephra particles within the peat. At the same time, four cores were taken along a transect of Plot 9 to investigate the horizontal variability of tephra. These treatments are summarised in Table 4.1.

The surface of the cores was taken to be the base of the green, photosynthesizing layer, sub-samples were taken at 1cm resolution from the surface to 10cm depth. Tephra samples were prepared from the nine cores following the method of Pilcher & Hall (1992) as described in section 5.3. To allow tephra shard concentration calculations a Lycopodium inoculum was added to the sample (Stockmarr 1971), a minimum of 200 Lycopodium grains were counted in the majority of samples and the number of tephra shards recorded.

To examine the microscopic distribution of tephra in the peat, thin sections were prepared from Plots 9 and 21. A 10x7cm thin-section tin was cut into a cleaned face of the extracted monolith. The samples were dried in acetone and then impregnated with crystic resin in a vacuum chamber. After impregnation, the samples were left to harden for six weeks. Samples were mounted on glass and ground to a thickness of approximately 25µm. This preparation was carried out at the Centre for

Table 4.1 Experimental treatment and sampling of plots

<table>
<thead>
<tr>
<th>Plot</th>
<th>Microform:</th>
<th>Treatment</th>
<th>Time of application:</th>
<th>Sampling:</th>
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<td>9</td>
<td>Low Hummock</td>
<td>50g tephra (&lt; 150µm)</td>
<td>May 2002</td>
<td>Monolith and cores after 13 months</td>
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<tr>
<td>15</td>
<td>Low Hummock</td>
<td>50g tephra (150-300µm)</td>
<td>May 2002</td>
<td>Cores at 5 intervals over 24 months</td>
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<tr>
<td>21</td>
<td>Hollow</td>
<td>300g tephra (&lt; 150µm)</td>
<td>June 2003</td>
<td>Monolith after 3 days</td>
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</table>

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Quaternary Research, Royal Holloway by Dr Aoibheann Kilfeather. The prepared thin-sections were examined at 400x magnification. Tephra shard identification is more difficult in these samples than in the ashed samples as the optical quality is somewhat poorer; shards are often partially obscured by organic material, may be shown in cross-section and cannot be moved or rotated. Due to these difficulties interpretation is based on clusters of shards. The clusters shown on Fig.4.3 are where two or more probable shards occur in a single field of vision. These clusters therefore highlight regions where tephra shards are present but provide only a semi-quantitative indication of overall tephra distribution.

4.3 RESULTS

To investigate the horizontal distribution of tephra within the plots, a series of cores were extracted from Plot 9 and examined for tephra. Four cores were extracted; cores 9-A, 9-B and 9-D are from lower elevation regions of the plot and core 9-C from a higher region of the plot. Tephra concentration and LOI plots are shown in Fig.4.1. All tephra profiles show a rapidly declining tephra concentration with depth, the majority of tephra shards remaining within the uppermost cm of peat. Core 9-C also shows a pronounced secondary tephra peak at 5-6cm. The maximum depth of tephra penetration varies from 3cm in cores 9-A and 9-D to 4cm in core 9-B and 6cm in core 9-C. Both the maximum and the overall concentrations vary greatly between cores. Much the greatest concentrations are found in core 9-B and particularly core 9-C with substantially lower concentrations in cores 9-A and 9-D. LOI plots for cores 9-A and 9-D do not show any distinct relationship to tephra concentration. However, the LOI in the uppermost cm of cores 9-B and 9-C is markedly reduced.

Fig.4.2 shows the results from Plot 15 investigating the vertical movement of tephra through the study period. In common with Plot 9, all tephra profiles show a rapid decline with the highest concentrations in the uppermost centimetre and tephra shards penetrating to 3cm (cores 15-B, 15-D and 15-E) or 4cm (cores 15-A, 15-C). Tephra concentrations vary greatly between the cores. There is a trend of increasing tephra concentration through the study period with gradually increasing values through the first four samples and a particularly dramatic increase to the final sample.
Fig. 4.1 Tephra concentration profiles (solid line) and loss on ignition (dotted line) through uppermost 10 cm of peat. Locations are labeled as distance from western margin of the sampling plot.
There is no apparent relationship between tephra concentration and LOI for cores 15-A to 15-D, however LOI in the uppermost cm of plot 15-E (79.6%) is much the lowest of any core examined here.

In nine investigated cores the overwhelming majority of tephra shards were contained within the uppermost centimetre of peat. The maximum depth of tephra shard penetration varied from 3 to 6cm and averaged 3.6cm. The smaller tephra shards in Plot 9 generally penetrated further than the larger shards in Plot 15. In all cores tephra concentration showed a rapid decay with depth. Secondary peaks were noted in core 15-A and 9-C. The secondary peak in core 15-A only represents a single shard and is therefore unimportant, however the secondary peak in core 9-C represents more shards and appears noteworthy. The majority of LOI profiles do not appear to show any relationship to tephra concentration, however the reduced values in the uppermost cm of cores 15-E, 9-B and 9-C may well represent the high tephra concentrations in these samples. The LOI values of around 95-97% in most of these samples are broadly typical of ombrotrophic peatlands.

Fig.4.3 shows thin-section images from Plots 21 and 9. The Plot 9 thin-section shows a relatively compact peat matrix. The peat contains fine channels (generally <5mm diameter) many of which have a roughly vertical orientation; these are most obvious in the lower half of the thin section. The centre of the slide contains a prominent root structure, which is most likely Calluna vulgaris. Tephra shards in this core are concentrated in the upper portions of the peat. Ten clusters were identified; these are all located on the right-hand side of the slide and reach a maximum depth of 5mm below the surface.

The thin-section from Plot 21, a Sphagnum-dominated hollow, shows a notably more porous structure than Plot 9. A sub-vertical band of large interconnected pores occupies the centre of the thin section. The slide bisects some roots but does not contain the large root structures of Plot 9. Tephra shards are widely distributed in this thin-section. The greatest concentration of clusters occurs on the left-hand side of the slide, approximately 5-13mm below the surface of the thin-section. A further six clusters occur towards the right-hand side of the slide between 14 and 32mm below the surface. Three clusters occur in the lower half of the slide at around 52, 68 and 74mm. It is interesting to note that all these lower clusters occur close to the channel feature in the centre of the slide.
Fig. 4.2 Tephra concentration profiles (solid line) and loss on ignition (dotted line) through uppermost 10cm of peat over the 24-month study period.
Fig. 4.3 Thin-sections from plots 9 and 21 showing location of tephra shard clusters
4.4 DISCUSSION

The results for horizontal distribution of tephra do not provide any significant evidence of tephra movement. Tephra shard concentrations are at their highest in the cores towards the centre of the plot (cores 9-B & 9-C) and lower in the peripheral cores (9-A & 9-D). The most likely explanation for this is unevenness in tephra application. During application, efforts were made to ensure even tephra application across the plot, however this is difficult to judge by eye and it is likely that areas at the centre of the plots received more. A further contributory factor may also be that tephra pathways through the overlying vegetation layer will serve to concentrate tephra in certain regions. These results provide no evidence for a horizontal movement of tephra towards the lower regions of the plot; concentrations are very similar in core B from a lower elevation point and core C from a higher elevation point.

The results from Plot 15 show a trend of increasing concentration through the two-year study period. The most likely reason for this is that tephra moved from the overlying vegetation (which was not included in tephra preparations) into the upper peat during the course of the experiment. However, results from Plot 9 suggest an uneven distribution of tephra across this plot, so it is possible that some of the apparent trend in Plot 15 is purely coincidental. Although tephra concentration increases over the study period, the tephra does not penetrate significantly further into the peat. The smaller tephra shards in Plot 9 penetrated further into the peat than the larger shards applied to Plot 15, presumably as the smaller shards can pass through smaller pores in the peat matrix and are less likely to be retained near the peat surface. This may suggest that tephra particle size can provide a further indication of the isochrone location, which may be particularly valuable where concentration profiles are complex.

The vertical distribution of tephra shown in these experiments would be reduced as peat accumulates and the tephra-containing peat is compressed on entering the catotelm. The large voids which occupy much of the thin-sections in these plots are absent from thin-sections taken from deeper peats, illustrating this compression.
The thin-section from Plot 9 is in general agreement with the pattern shown in the concentration plots. All tephra clusters located in this slide occur in the uppermost cm of peat. Given the smaller volume of material in the thin-section compared to the ashing preparations it is unsurprising that the ‘tail’ of declining tephra concentrations with depth is not represented in these results. The thin section sample from plot 21 shows a rather more complex pattern. In this thin section tephra penetrates significantly further into the peat, this has occurred over a very short period of time. The lowest shards recovered lie close to what appears to be a vertical channel, this is interesting as it suggests that such features may provide pathways through the peat. On the left side of the thin section, the greatest concentrations are in the uppermost cm, in keeping with results from other plots. However, on the right-hand side of the thin section, the greatest concentrations are somewhat below the surface, the reason for this difference is unclear. The greater tephra penetration in this thin-section is most likely due to the Sphagnum-dominated vegetation and more porous peat structure. Although it is possible that some distortion of tephra distribution has occurred during sample preparation, there is no indication that this has taken place.

By comparison to the results of Clymo & Mackay (1987), it appears that vertical movement of tephra through peat is probably no greater than that of pollen and possibly rather less. However the differences in methodology and peat composition make an accurate comparison difficult. Due to the angular morphology and sharp edges of tephra shards it would seem reasonable to suppose that tephra are less liable to movement than generally sub-rounded pollen grains. Hall & Pilcher (2002) have suggested that tephra profiles may aid interpretation of other signals such as pollen. This may be true, however pollen and tephra particles cannot be assumed to react in the same way to environmental conditions. It seems likely that where a tephra profile is complex this may urge caution in interpretation of pollen signals, however a simple tephra profile cannot be taken as indication that pollen taphonomy is also simple.

Overall, the results provide generally good support for the use of tephrochronology in peatlands. In the majority of cores and plots, tephra remains in the uppermost centimetre of peat producing an isochrone which accurately represents the location of the peat surface at the time of tephra-deposition. However, some results are more complicated; core 9-C shows a secondary tephra peak and the thin-
section of Plot 21 shows a complicated tephra distribution. The reasons for these complications are uncertain and will require further work. These results suggest that it is justified to use tephra layers as direct evidence of volcanic eruptions in the peat column and that it should be possible to relate tephra layers to the palaeoecological record to investigate volcanic impacts.

### Key Findings

- Tephra does move down through peat but this movement is limited.
- Tephra taphonomy may be affected by peat micro-structure.
- It seems generally justified to use tephra layers to investigate volcanic impacts on the palaeoecological record.
CHAPTER 5. PALAEOENVIRONMENTAL METHODS

5.1 LOCATION AND SITES

The palaeoenvironmental studies in this thesis have two main requirements for site selection:

- Numerous volcanoes capable of producing distal impacts and causing climate change.
- Numerous peatlands, preferably raised, ombrotrophic bogs

The first requirement necessitates that the area must be adjacent to an oceanic margin, as the most explosive, climatically effective volcanic eruptions are produced at subduction zones. Given this requirement, a natural choice of location is the Pacific Rim where most of the world's subduction zone volcanoes are located.

Peatlands are widely found in the temperate northerly and southerly latitudes. This therefore leads to four main candidate areas where appropriate volcanoes and suitable peatlands co-exist, these are: New Zealand, southern South America, the Asian North Pacific, particularly Kamchatka, and the Pacific Northwest of North America. North America and specifically Alaska was selected for this study. Over 45% of the state of Alaska is classified as wetland. Included in this are a large number of Sphagnum peatlands; the vast majority of these have received little human impact (Dachnowski-Stokes 1941, Hofstetter 1983, Halsey et al. 2000). Alaska also makes a suitable location, as there is a pre-existing body of literature on the tephrochronology of the area. In particular the region contains tephra from some very large events such as the c.3400BP caldera-forming eruption of Aniakchak (Miller & Smith 1987, Richle et al. 1987, Begét et al. 1992). Climate observations following several recent eruptions have shown that Alaska may be particularly sensitive to volcanic-forced climate change (Robock 2002).

5.1.1 Volcanoes of Alaska

Alaska contains over 100 Quaternary volcanoes, 44 of which have erupted in historic times (Richter et al. 1995a). This represents around 8% of the world's active above-water volcanoes. Alaska's volcanoes are formed by the subduction of the Pacific...
plate under the North American plate. The majority of the volcanoes occur in the
Aleutian arc, the long chain of volcanoes which extends from the Cook Inlet down the
Alaska peninsula and the Aleutian islands eventually to Kamchatka (Rennick 1991). This
chain forms the northern section of the so-called Pacific 'ring of fire'. A second smaller
group of volcanoes occurs in the Wrangell Volcanic Field further east in Alaska and
isolated volcanoes occur elsewhere in the state. Several of these volcanoes and the tephra
layers they have produced are worthy of further discussion.

The White River Ash and Mount Churchill

The White River Ash (WRA) is a distinctive light-coloured tephra layer found
throughout much of eastern Alaska and western Canada (Lerbelano & Campbell 1969;
Fig. 5.3). The tephra layer actually represents two eruptions. The more voluminous
Eastern lobe is the younger of the two (c.1147 cal. BP; Clague et al. 1995). This tephra
covers approximately 540,000Km² representing a volume of at least 27Km³ (Robinson
2001). By this criteria it ranks as one of the most voluminous pyroclastic eruptions in
North America in the past 2000 years (Richter et al. 1995a). The Northern Lobe tephra is
less extensive and is dated to about 1890BP (Lerbelano et al. 1975). The tephra layers
provide valuable isochrones for palaeoenvironmental and geomorphological research in
Workman (1979) and Moodie et al. (1992) have suggested that these eruptions may have
had significant impacts on the prehistoric human occupation of the region.

There has been some controversy over the source of these tephras within the
Wrangell Volcanic Field (WVF). Early workers assumed the prominent Mt Natazhat was
the source however this now seems unlikely. Lerbekmo & Campbell (1969) located a
pumice mound on the margin of the Klutlan Glacier which they suggested marked a
source vent. However, Richter et al. (1995b) showed that pumice deposits at this site
were relatively thin compared to surrounding areas. They sampled pumice deposits from
the crater rim of adjacent Mt. Churchill and demonstrated geochemical correlation with
WRA deposits strongly suggesting this as the source. Mt Churchill has been
acknowledged as the source for over a decade; however new findings are now
challenging this. Recent ice core drilling on the col between Mt. Churchill and Mt. Bona revealed no WRA layer in a record which was believed to span the period of the younger eruption (Personal Communication, Prof. L. Thompson, Ohio State University). If this finding is substantiated then it seems that new theories will be needed to explain the source of the tephra.

Aniakchak

Another Alaskan volcano capable of extremely large eruptions is Aniakchak volcano in western Alaska. This volcano is a spectacular caldera 10Km in diameter and over 1Km deep, located in the middle of the Alaska Peninsula (Miller & Smith 1987). Over 20 eruptions are believed to have taken place in the last 3500 years (Neal et al. 1992); the only historic eruption in 1931 is relatively well documented. Historical records include accounts of acid damage associated with tephra deposition (Rennick 1991, Neal et al. 2001).

Probably the largest Holocene eruption from Aniakchak is the caldera-forming event around 3500 BP, Miller & Smith (1987) estimate the size of the eruption at over 50Km$^3$. This event is probably the largest Alaskan eruption of the late Holocene and one of the largest in the world in this period (Begét et al. 1992). Pyroclastic flows from the eruption extend more than 80Km from the volcano to the coastal plains (Miller & Smith 1987). Airfall tephra from the eruption has been found over 1500Km to the north (Riehle et al. 1987, Begét et al. 1992). This eruption probably had extreme impacts upon the Alaska peninsula with a devastating impact on vegetation and human occupation of the region (VanderHoek & Nelson 2003, VanderHoek & Myron 2004). Waythomas & Neal (1998) document evidence for a pyroclastic flow-generated tsunami which would have had substantial impacts on the northern shore of Bristol Bay.

A subject of great debate over recent years is the extent to which Aniakchak may have had a global impact. The Aniakchak eruption is currently dated by radiocarbon to around 1690 cal. BC given dating errors the actual age may be nearer to 1650 cal. BC (Begét et al. 1992). In this period several palaeo-records have indicated a period of rapid climatic change caused by a volcanic eruption. In north American dendroclimatic records
Lamarche & Hirschboek (1984) report anomalous frost rings dated to 1626 cal. BC and in northern Ireland Baillie & Munro (1988) report anomalous narrow rings around 1628 cal. BC. A notable acid peak in the Dye 3 greenland ice core has been dated to around 1645 cal. BC and another to 1627/8 cal. BC in the GISP-2 core (Hammer et al. 1987, Zielinski & Germani 1998). All of these events have previously been attributed to the infamous 'Minoan' eruption of Santorini. However whether this is truly justified is a subject of much debate. Recent studies have highlighted other large eruptions within this time-frame including eruptions of Vesuvius and Mt. St. Helens as well as Santorini and Aniakchak (Vogel et al. 1990, Begét et al. 1992, Melekestev & Miller 1997). It has also been noted that there is actually a considerable spread of dates in the palaeo-record (Pyle 1989) so it is possible this may not be a single event at all.

The Santorini eruption is quite poorly dated by direct means. Initially the eruption was dated by archaeological inference by comparing pottery styles from the buried settlement of Akrotiri to pharaonic Egypt. However both the correlations and the Egyptian dates themselves are far from certain and lead to a span of dates of over 150 years (Hammer et al. 1987, Manning 1988). Radiocarbon dating of preserved material at the site has been inconclusive, calibrated dates spanned a period of 600 years while even a narrow interpretation excluding all possible outliers produces an age-range of 66 years (Hammer et al. 1987, 1988, Manning 1988). The dendroclimatic and ice-core dates do not agree well with this direct dating evidence (Cadogan 1987, 1988). Recently it has seemed that a conclusive answer may be possible with the discovery of small quantities of tephra associated with the 1628/1627BC SO$_4^{2-}$ spike in the GISP-2 ice core (Zielinski & Germani 1998). The geochemistry of this tephra was not thought to match that of Santorini, although this has now been disputed by Manning (1998). Most recently tephra has been recovered from the GRIP core by Hammer et al. (2003). There has been debate in the literature as to the extent to which the geochemistry of this tephra agrees with those of the major eruptions. Hammer et al. (2003) considered that the data supported a Santorini origin but Pearce et al. (2004) re-analyzed Aniakchak samples to suggest this was a more likely source (Eastwood et al. 2004). This debate is still not decided, the most recent contributions suggests that no firm conclusions can be reached but that Aniakchak is the most likely of the four major suspects (Keenan in press). I consider there is more
evidence for the cataclysmic scale of the event for Aniakchak than any of the alternatives. However, it is clear that several eruptions occur in a relatively confined period of time and combined impacts from several events cannot be excluded for some of the suggested effects.

**Katmai-Novarupta**

The Novarupta vent adjacent to the volcano Mt Katmai was the site of the 20th century’s most voluminous volcanic eruption (Hildreth 1983, Hildreth & Fierstein 2000). The eruption from 6-9th June 1912 produced 30Km$^3$ of tephra and 11Km$^3$ of pyroclastic flow deposits. Visible tephra-fall was detected as far away as the Puget Sound region (2400Km; Wilcox 1959) and dust veils as distant as Greece and Algeria (Hildreth & Fierstein 2000). Pyroclastic flows travelled northwest covering an area of 120Km$^3$ in deposits up to a depth of 250m, this area has become known as the Valley of Ten Thousand Smokes.

Proximal impacts of the eruption were extreme. In the Valley of Ten Thousand Smokes all vegetation was rapidly destroyed while further away vegetation was buried in thick tephra deposits. In the proximal areas re-vegetation has been slow and large areas remain vegetation free to today. Impacts on vegetation seem to have been dependent on precise location, Wilcox (1959) comments that Alders on slopes facing the volcano were much more effected than on slopes facing away. On Kodiak Island a 10-inch tephra layer seems not to have killed most trees. Re-vegetation was noted to be taking place by one year after the eruption and was complete by three years after the eruption. Many plants were able to grow through the tephra layer rather than recolonizing from scratch (Griggs 1918, 1919). There appears to have been little impact due to chemical action, most reported impacts were thought to be purely due to the physical action of the tephra,
South-central Alaska sites. See text for site codes.

Solid squares show sites where short surface cores were extracted. See detailed maps for higher resolution location of Southcentral and Southeast Alaska. Solid circles show sites where cores or long sections were extracted. Open circles show surface sample sites.

Fig. 5.1 Sampling sites in Alaska. Solid circles show sites where cores or long sections were extracted. Open circles show surface sample sites.

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primarily by burial. At distance from the volcano Wilcox (1959) describes reports of ‘corrosive rains’ from Seward, Cordova and Cape Spencer in southern Alaska and even at Vancouver, British Columbia.

5.1.2 Sites

Sites were sampled throughout Alaska. For the purposes of description, the sites are divided among three general regions- Southeast Alaska including sites around Juneau and Haines, South-central Alaska including sites on the Kenai Peninsula and further north, and Western and Interior Alaska including sites on the Seward Peninsula, a site in southwest Alaska and sites around Fairbanks and east along the Alaska Highway (Fig. 5.1). Tephra layers are found in sediments across Alaska. Tephra layers have been documented in all of the general regions visited in Alaska, if not in the areas where sites were sampled. These regional tephrochronologies are outlined briefly in the following sections.

Sites were selected by several criteria. Peatlands were chosen for an ombrotrophic appearance with raised bogs preferentially selected as these are most sensitive to climatic change. Although peat cutting is not prevalent in Alaska, several of the visited sites did show signs of anthropogenic disturbance- principally through off-road driving. These sites were avoided for palaeoecological study although two sites with some disturbance were included in the transfer function study. Sites were selected for a maximum depth of peat to provide the highest resolution possible.

5.1.3 Southeast Alaska

Five sites were selected in the Juneau and Haines regions of Southeast Alaska (Fig.5.2). This area was selected as the high rainfall and mild climate made it likely to contain intact ombrotrophic bogs (Rigg 1914, 1937, Hofstetter 1983). Vegetation of the sites is similar, including *Empetrum nigrum, Eriophorum* spp., *Oxyccoccus microcarpus, Cornus canadensis, Cladonia portentosa* and extensive *Sphagnum* carpets.
Fig. 5.2 Peatland sites in southeast Alaska
Southeast Alaska is comparatively distant from the bulk of the Alaskan volcanoes but does contain one Quaternary volcano, Mt Edgecumbe (Edgecumbe Volcanic Field: EVF) located on Kuzof Island near Sitka, c. 200Km southwest from Juneau (Fig. 5.3). The only well-known regional tephra isochrone is from a Younger Dryas age (c.11,250 $^{14}$C aBP) Mt Edgecumbe eruption (Begét & Motyka 1998). Tephra from this eruption has been found from Juneau, to Yakobi Island (c.150Km west of Juneau) and at Glacier Bay National Monument (c.150Km northwest from Juneau; Fig. 5.3; McKenzie 1970, Riehle et al. 1992, Begét & Motyka 1998). The Holocene volcanic activity of Mt Edgecumbe remains poorly known. Riehle & Brew (1984) and Riehle (1996) suggested there were two eruptions around 4-6000BP. The extent of these eruptions is unknown; to date, deposits have only been found within 75Km of Kruzof Island suggesting they were relatively minor events (Riehle et al. 1992).

Despite the effective absence of a Holocene tephrochronology for the region it was considered likely that micro-tephra layers would be present. Southeast Alaska is relatively close to the Wrangell Volcanic Field. The sites near Haines are within around 100Km of the limit of visible deposits of White River Ash (Robinson 2001); it therefore seemed probable that microscopic deposits might be present here. The prevailing wind directions may also serve to direct tephras from more distant volcanoes in southcentral and southwest Alaska towards the region.

**Point Lena (LNA)**

This site has been previously described by Dachnowski-Stokes (1941: referred to as ‘Lena Beach’). The site lies at 58°23’08”N 134°44’39”W in a small area of flatter land between the Coast Mountains and the sea (Favorite Channel) adjacent to Point Lena. Miller (1975) mapped the site as part of his more general mapping of the surficial geology of the Juneau region. The site is a raised bog approximately 200m wide by 300m long. The site is noticeably domed in profile and is clearly ombrotrophic. It is bordered by Glacier Highway and Lena Cove Road on two sides and surrounded by coniferous woodland. Stunted conifers and small ponds occur in localized areas of the bog. A core, 530cm long was extracted from near the centre of the bog.
Eaglecrest (ECR)
This site lies around 58°20'00"N 134°33'36"W on the western side of the Fish Creek valley towards the northern end of Douglas Island. The site has been mapped by Miller (1975) and is approximately 700m long by 300m at its widest. The Fish Creek road cuts across the northern end of the site. The mire has a slight slope to the north and little evidence of convexity in profile. This peatland is similar in morphology to European blanket bogs. The maximum depth of peat found at the site was 375cm towards the Northwest of the peatland; a core was extracted from this location.

Spaulding Meadows (SPM)
This site lies around 59°24'01"N 134°39'40"W in the valley of the Waydelich Creek above Auke Bay on the northern shore of Stephens Passage. The site is included in the map of Miller (1975) and is approximately 700m long and up to 300m wide. The peatland is at an elevation of about 250m. The site is on a distinct gradient and may not be entirely ombrotrophic. A 206cm long core was taken from the southern end of the site.

Chilkoot Pond (CHP)
This site lies at 59°19'20"N 135°33'50"W on the isthmus of land dividing Lutak Inlet from Chilkoot Lake in the Haines region. The site is a small peatland (less than 100m long) occupying a clearing in dense coniferous woodland. A single large pond covers much of the area; the peat deposits may represent partial infilling of this pond. Peat is relatively shallow; a core was taken from the maximum depth at 185cm.

Mount Riley (MTR)
This site is at 59°11'23"N 135°23'04"W very close to the top of Mt Riley (536m) on the Chilkat peninsula. A small muskeg occupies a shallow basin just north of the summit. A 220 cm core was taken from the deepest part of the mire towards the eastern side. This site is within 3Km of Lily Lake, from which a late quaternary vegetation history has been reconstructed by Cwynar (1990).
5.1.4 South-central Alaska

Seven sites were sampled in Southcentral Alaska as part of the testate amoebae transfer function, as described elsewhere. In addition to the surface samples, cores were extracted from the Moose Pass (MP) and Sterling (ST) sites (Fig. 5.1). These sites are Sphagnum-dominated peatlands with visible (mm-scale) tephra layers. A 150cm core was extracted from the center of the Moose Pass mire and a 93cm core from the northern margin of the Sterling site. These sites are relatively close to the volcanoes of the Cook Inlet and can be used to examine proximal volcanic impacts as a contrast to the distal sites.

South-central Alaska is one of the most volcanically active regions of the state. Five volcanoes occur near to the field sites along the western side of the Cook Inlet; Augustine, Iliamna, Redoubt, Spurr and Hayes volcanoes (Fig. 5.3). Further volcanoes occur further south along the Alaska Peninsula and may have deposited tephras in the region. Given the number of volcanoes, the tephrochronology of the region is inevitably complex. In the areas closest to the volcanoes tephras are highly numerous, often poorly preserved, frequently inter-mixed and sometimes heterogeneous in composition (Begét & Nye 1994, Riehle et al. 2000). These problems are most acute to the south of the Cook Inlet where volcanoes are most concentrated and tephrochronology is all but impossible (Riehle et al. 1999, 2000). The tephra layers of the upper Cook Inlet have been investigated by Riehle (1985). His results show numerous Holocene eruptions of the volcanoes in this region; around 6 to 8 eruptions of Hayes, around 35 of Spurr, 30 of Redoubt and several of Augustine volcano. The deposits of most of these eruptions are restricted to the western side of the Cook Inlet. On the Kenai Peninsula, there are markedly fewer known tephra layers. Riehle (1985) investigated two sites on the Cook Inlet shoreline and found up to five visible tephra layers. Begét et al. (1994) investigated the tephrostratigraphy of sediments from Skilak Lake on the central Kenai peninsula, approximately 10Km south of the Sterling site and 40Km west of Moose Pass. Several non-visible late Holocene tephras were detected using magnetic susceptibility including layers from Katmai, Augustine and several from Spurr and Redoubt.
5.1.5 Interior & Western Alaska

Three sites were sampled in western Alaska and a further five in Interior Alaska. These more northerly sites are different in peat structure and vegetation from the sites in southern Alaska. The vegetation is generally sedge dominated with much less, if any, *Sphagnum*. The peat is often highly humified and fibrous, there is evidence for cryoturbation in some of the sites. These sites are generally less optimal for palaeoecological analyses.

In western Alaska the most widespread tephra layer is from the Aniakchak caldera, this is the only known tephra layer in northwest Alaska. Tephra from this volcano is ubiquitous towards the south of the region and present in sites north along the Pacific seaboard (Riehle et al. 1987). The most northerly sites it has been encountered in are in the north of the Seward Peninsula (Bégét et al. 1992; Fig. 5.3).

In Interior Alaska several tephras are found from volcanoes in southern Alaska. The Jarvis Ash (C.3660 BP) is a widely dispersed deposit from Hayes volcano found in numerous sites as far north as Denali NPP (Riehle et al. 1990, Bégét et al. 1991b, Child et al. 1998). Child et al. (1998) have also identified the C.6000 BP Oshetna tephra and an unknown basaltic tephra (possibly from Mt Spurr) from a site in Denali NPP. The White River Ash is found across large areas of eastern Interior Alaska (Downes 1985, Robinson 2001; Fig. 5.3).

**Ahklun Mountains (AKH)**
This site is a small ombrotrophic mire in the Ahklun Mountains of southwest Alaska around 160°45°W 59°30’N. The site was sampled by Darrel Kaufman & researchers from Northern Arizona University as part of more general Quaternary field research in the region. A prominent 11cm thick tephra layer is present in the core.

**Kougarok (KOU)**
This site lies in the central Seward Peninsula in Northwestern Alaska at 65°23’15”N, 164°33’49”W. A 150cm monolith was extracted from a raised peat bank at the edge of a small pond. The pond is probably the remnant of a relict palsa; the peat bank from which
the monolith was extracted is currently water-shedding and is likely to have been so for some time. The peat is lightly humified with monocot and *Sphagnum* remains. The stratigraphy shows some evidence for cryoturbation but this is not extensive. No tephras were located and the site has not been subject to palaeoecological work.

Espenberg (ESP)
This site lies south of Cape Espenberg on the northern Seward peninsula at 66°28′22″N, 163°56′56″W. The site is a large palsa mire on the edge of one of the numerous small lakes which cover this region. A 160cm monolith was extracted from an open exposure at the lakeside. The peat is moderately humified and sedge-dominated, with some evidence of cryoturbation. One visible tephra layer is present at approximately 40cm depth.

Dot Lake B (DLB)
This site lies in eastern interior Alaska at 63°40′29″N, 144°05′47″W, to the north of the Alaska Highway. The surface vegetation of the site is *Sphagnum*-dominated although the peat becomes monocot dominated lower in the section. One microtephra was found in this site, the only tephra found in the interior Alaska sites.

Other sites
Four other sites were sampled in interior Alaska:
ABS (64°03′53″N, 149°16′27″W) is a sedge dominated peatland situated in hilly terrain approximately 140Km south of Fairbanks. A 50cm monolith block was extracted.
TCB (64°13′29″N, 146°00′31″W) is a sedge tussock peatland situated near to the Alaska Highway, east of Fairbanks. A 50cm monolith block was extracted.
DB (62°41′53″N, 141°08′24″W) is a sedge tussock peatland with scattered trees and shrubs approximately 150m south of the Alaska Highway, east of Fairbanks. A 50cm monolith block was extracted.
DL (63°33′26″N, 143°52′59″W) is a sedge-dominated tussock peatland with scattered shrubs, approximately 50m south of the Alaska Highway. A 50cm monolith block was extracted.
All these sites are sedge dominated with very prominent tussocks. The sites are in a region of permafrost and were frozen at around 50-100cm depth. No tephras were located in the cores and these sites have not been extensively investigated.
5.2 FIELD METHODS

A single core for palaeoecological analysis was extracted from each site. Although this approach is obviously less preferable to a section (e.g. Barber 1981) or a multiple core (e.g. Svensson 1988a&b) approach previous studies suggest that major changes are usually synchronous between cores taken from the same site (Barber et al. 1998). The sites were repeatedly sampled with a 20mm auger to find the maximum depth of peat. Where the site appeared particularly promising, the stratigraphy of these cores was recorded. Surface vegetation of all sites was described and surveyed using multiple quadrat counts (Rodwell 1991). Sampling locations on the selected sites were chosen for a maximum peat depth and in climatically sensitive lawn microforms where possible. Cores for palaeoecological analyses were extracted using a 5cm diameter, 50cm long Russian corer to minimize disturbance of the peat (Barber 1984, Aaby & Digerfeldt 1986). Extracted cores were placed in plastic gutter tubing and wrapped in plastic. The corer was cleaned after every core taken. Twin adjacent cores were taken and cores were overlapped by 5cm using two separate boreholes for each core. A monolith block (approx. 10x10x30cm) was extracted from the surface where the peat was not solid enough to allow coring. Exceptions to this sampling methodology were the sites in Western and Interior Alaska. At these sites, monolith blocks were extracted from exposed sections (Kougarok and Espenburg sites) or cut-down into the peat from above (other sites). The samples were packaged whole and returned to the UK for analysis in the laboratory.
5.3 TEPHRA METHODS

The term ‘tephra’ refers to all airborne pyroclastic material. The finest fraction of this tephra (often referred to as ‘volcanic ash’) can remain in the atmosphere for a period of several months, and spread to cover a large area. Tephra has been used in many palaeoecological studies as it provides a time-specific marker horizon (isochrone), this may allow comparison between sites and, where the age of the eruption is known, a means of dating sediments.

Tephrochronology has been widely utilised over the past century or more, mostly in areas immediately adjacent to volcanic source regions such as Iceland, Alaska and New Zealand (e.g. Begét et al. 1991a, Begét & Motyka 1998, Newnham et al. 1998, Wastegård et al. 2001). In these areas, tephra layers are usually large and readily identifiable by eye. More recently, methods have been developed which allow the use of tephrochronology in areas considerably more distant from the source regions. Non-visible micro-tephra layers (also termed ‘cryptotephras’) have been recovered from peatlands at great distances from their volcanic sources. In the UK micro-tephra layers were first discovered by Dugmore (1989) at Altnabreac in Caithness, northern Scotland. Since this discovery, a large number of small tephra layers have been found across the UK, over 1500Km from their sources in Iceland. More than ten Holocene tephra isochrones have been found, extending at least as far South as Northern England and North Wales (Pilcher et al. 1995, Dugmore et al. 1995, 1996, Pilcher & Hall 1996, Langdon & Barber 2001, 2002, Hall & Pilcher 2002). This work illustrates the potential to expand tephra study in other areas of the world where only visible layers have been studied. This could allow a better understanding of the impacts of these eruptions as well as an increased potential for tephrochronology.

Peatlands are particularly useful media for tephrochronology. Peatland surfaces are wet and well vegetated and therefore effective at trapping and preserving atmospherically deposited tephra (Zoltai 1988, Robinson 2001). Tephra shards found in peatlands are well preserved and appear to have undergone minimal alteration over the last 6000 years or more (Dugmore et al. 1992). The geochemical composition of tephra is
usually unique to a source volcano and often to a source eruption. Geochemical analysis of tephra layers allows correlation of tephras between sites, to source and to eruption. In tephrochronology, the tephra is usually characterized by the major element geochemistry of volcanic glass shards. Glass shards are formed by rapid cooling of magma and are generally representative of the bulk geochemistry of the magma body (Hunt & Hill 1993). Glass shard geochemistry is usually homogenous through an eruption although compositional changes have been noted in some eruptions (e.g. Downes 1985). In the eruptive plume glass shards generally travel further than heavier minerals and are often the only tephra component encountered in distal tephra studies. However, in proximal deposits, mineral phenocrysts may be highly abundant and density-separation methods may be required to isolate glass shards.

Several methods have been used to examine the geochemistry of tephras, the most widely used technique is electron probe microanalysis (EPMA) and particularly its wavelength dispersive variant. Essentially the approach works by bombarding the samples with an electron beam. The sample composition is determined as the X-ray energy released is unique to each source element and their intensity is proportional to the amount of an element present (Hunt & Hill 1993). Further discussion of the analytical methodology and practical issues are given by Sweatman & Long (1969), Froggatt (1992) and Hunt & Hill (1993, 2001).

Conventionally, location of tephra layers within a peat sequence has been achieved using preparation methods to remove organic material followed by meticulous microscopy. The simplest method of removing organic material is by ashing. This method relies on the very high organic content of peat. The sample is combusted at high temperatures and the residue is then cleaned and examined microscopically for the presence of tephra. As peatlands, unlike most lake sediments, contain little inorganic material (Rose et al. 1996), a high proportion of the residue may be tephra. This method is rapid and effective but has the problem that the extreme heating used is believed to alter tephra geochemistry (Dugmore et al. 1992). An alternative method is acid-digestion; this method removes organic material by wet oxidation leaving the inorganic fraction. The method produces clean samples (often rather better than ashing) that are directly ready for EPMA, but is both more time-consuming and more costly.
For these reasons, there has been a recent emphasis on non-destructive scanning methods for detecting tephra in peat. Dugmore & Newton (1992) used X-radiography to investigate a tephra layer in peat. Their methodology provides a rapid and non-destructive method of locating tephra layers by using X-rays to detect structural and density variations in the peat invisible to the naked eye. Similarly, Caseldine et al. (1999) used light reflectance and luminescence properties to detect small tephra layers in peat. Both of these methods may prove valuable because as well as enabling rapid location of tephra layers, they also allow investigation of the horizontal and vertical spread of tephra (as discussed previously). However these methods have not been widely used due to problems of equipment cost and availability, high detection limits and possible problems with distinguishing tephra from other mineral material. Although microscopic investigation for tephra is time-consuming, this method remains the most used—principally due to its greater simplicity and lower detection limits.

Problems and issues with the method

Some persistent problems with the method remain unresolved. Use of tephra as a dating tool can be complicated where a) the geochemistry of the tephra layers are not distinctive and b) where the age of the eruption is unknown or inadequately dated. EPMA to determine geochemical composition faces several methodological problems. Problems can be caused by a variety of factors including instrumental problems, poor sample preparation, standardization and analytical procedures (Hunt & Hill 1996). A particular problem is the loss of sodium by migration and volatilization under electron bombardment (Froggatt 1992). Inter-laboratory comparison exercises suggest there are notable differences between the results of different microprobes centres (Hunt & Hill 1996, Hunt et al. 1998). Standardized approaches should be adopted to minimize these problems (Froggatt 1992, Hunt & Hill 1993, 1996).

The taphonomic processes of tephra incorporation in peat are poorly known. The experiments described in Chapter XX suggest that tephra movement is probably limited in extent but may be controlled by the microscopic structure of the peat. The limited nature of these experiments means there is still some concern over tephra migration; this
might cause problems in precisely linking the palaeoecological record to the age of the volcanic event.

Role of the method in this study

In this study tephrology fulfills several key roles. Firstly and most importantly, tephra layers allow precise positioning of a volcanic event in terms of the peatland palaeoeccological record. This allows the use of a precise stratigraphic approach to investigate any impacts upon the peatland. Identification of the tephra layer to source eruption is important as it allows an assessment to be made of the likely affects of that eruption in terms of direct and indirect (climatic) impacts upon the peatland. If it is possible to correlate tephras with dated eruptions this will also allow comparison of results with other palaeoeccological and palaeoclimatic records from both the immediate region and further afield. This will reveal further information about the spatial dynamics and modes of impact of any volcanic effects. Finally, if multiple tephra layers from eruptions of known age are present within a peat core it is possible to develop an age-depth model which is valuable to investigate the duration of any volcanic impacts as well as to date the full core humification record.

Practical methodology

In this study an ashing method was used to locate the tephra layers followed by acid digestion and EPMA to examine the geochemistry of identified layers. The ashing methodology was based on that of Pilcher & Hall (1992). Contiguous 5cm samples were burned in a furnace at 550°C, samples were weighed pre- and post-burning and this data used to calculate loss on ignition (LOI) which can provide an aid to identifying the largest layers and is also useful for humification analyses. The remaining inorganic residue was added to a 25ml centrifuge tube with 5ml of 10% HCl and centrifuged for 5 minutes at 3000 RPM. Following Caseldine et al. (1998) a Lycopodium inoculum was added in this stage to allow a quantitative count of tephra shards. Centrifuge tubes were topped up with distilled water and the sample centrifuged for a further 5 minutes. The
supernatant was then decanted off, further distilled water added and the sample
 centrifuged again for a further 5 minutes. The prepared sample was stored in a 5ml glass
 vial. Slides were prepared by mixing a drop of the prepared sample with a drop of
glycerol on a clean microscope slide. Tephra slides were examined microscopically at
400x magnification. Tephra shards were distinguished from other inorganic material and
biogenic silica by their distinctive morphology, vesicularity and colour. Where significant
numbers of tephra shards were identified, the core was sub-sampled at 1-cm resolution
and the preparation repeated as above to locate the region of peak concentration and
produce a concentration profile. In the sites from southcentral Alaska visible tephra
layers were present and tephra shards were present through most of the cores. Only the
visible tephras were studied from these sites.

Samples were prepared for EPMA from all major tephra zones. An acid-digestion
method was used to avoid altering the geochemical structure of the tephra. Methodology
follows the standard procedure as described on the TephraBase website
(http://www.geo.ed.ac.uk/tephra; University of Edinburgh), based on the methods of
Persson (1971) and Dugmore (1989). A 1-2 cm³ piece of tephra-containing peat was
broken up and placed in a 150ml conical flask. 50ml of concentrated sulphuric acid was
added and the flask shaken, several ml of concentrated nitric acid were gradually added
to the solution. The conical flask was placed on a hot-plate and the solution heated until it
turned a clear yellow colour. At this point the sample was removed from the hot-plate and
allowed to cool. Once cool, the sample was topped up with distilled water and left for the
sediment to settle for at least an hour. The supernatant was decanted off and the sample
poured into a centrifuge tube. The sample was centrifuged at 3000RPM for 5 minutes.
The supernatant was then poured off and the sample topped up with distilled water. The
sample was centrifuged, decanted and topped up and then centrifuged again. The residue
was stored in 5ml vials in distilled water.

This three-stage preparation process has been used in many recent studies and
performs well (Pilcher & Hall 1992, Langdon & Barber 2004). However the method is
both time-consuming and uses a lot of material (typically 3cm³ per 1cm core depth),
which limits the availability of material for palaeoecological analyses. There is therefore
an incentive for developing preparation methods that are quicker and more efficient. In
this study the possibility of preparation based on microwave-digestion was investigated, these experiments are described in Appendix I. Non-destructive scanning methods may also have a greater role to play in developing peatland tephrochronology. A few samples were examined using field-portable x-ray fluorescence analysis (FP-XRF) however preliminary results suggested that unlike conventional XRF equipment (Lowe et al. 1980), this equipment is inadequate for detecting small tephra layers in peat. The particle size of large visible tephra layers was investigated using laser-diffraction particle size analysis (LD-PSA). Large peat samples were acid-digested based on the method used for EPMA samples. Samples were analysed using a Beckman Coulter LS 13 320 machine following standard methods.

Thin-sections for EPMA were prepared following standard methods (Dugmore et al. 1995). The acid-digested tephra was added drop-by-drop to a heated, roughened slide and left for the liquid to evaporate. The tephra was mixed with a small amount of epoxy resin (araldite) and left to cure for two hours. The resin layer was ground down using successively finer grit-papers and polished using 6μm and 1μm diamond pastes, before being carbon coated. The samples analysed at the University of Bergen were prepared at the University of Iceland (smaller samples) and the Department of Earth Science, University of Bergen (larger samples). Preparation methods for these samples are slightly different although these differences are unlikely to be important.

All prepared samples were analysed using wavelength dispersive EPMA. Two machines were used, each with slightly different operating conditions although both machines were well standardized. Samples with a ‘B’ notation were analyzed using the ARL-SEMQ microprobe at the Department of Earth Science, University of Bergen. Operating conditions were a 15KV accelerating voltage, 10nA beam current, and a 1μm beam. Samples with an ‘E’ notation were analysed on the Cameca SX100 microprobe at the School of Geosciences, University of Edinburgh using a 20KV accelerating voltage and 4nA beam current. Where shard size permitted, the beam was rastered over a 10x10 or 5x5μm grid to minimize sodium loss, although for many samples this was not possible and a static 1μm beam was used. P2O5 was measured in one set of analyses on the Edinburgh but not at Bergen. Values are generally low and have not been considered in correlating tephras. For the visible tephra layers, totals of less than 95% were not
accepted following Hunt & Hill (1993). However with the microtephras from southeast Alaska, totals are generally low, probably due to shard hydration. For these tephras a slightly lower limit of 94% was applied.

Data Analysis

To examine the correlation between tephras found in this study and those previously examined a variety of graphical and statistical methods were investigated. Plots and ternary diagrams were constructed for selected major oxides. The most intensively used statistical technique was similarity coefficients (Borchardt et al., 1972). This is a technique for comparing average percentages of major oxides between tephra pairs. The method is widely used in areas where tephra layers are highly numerous and particularly in Alaska. The similarity coefficient (SC) is calculated as the averaged ratio of normalized oxides using the lesser value as the numerator. Following Riehle (1985) oxides with a maximum value of less than 0.4% are excluded from the calculation. Beget et al. (1992) considered that a SC of ≥0.95 shows exact correlation, Riehle et al. (1992) note that SCs as low as 0.97 can be due simply to instrumental variability. Beget et al. (1992) consider that a SC of 0.90-0.94 may indicate a different tephra from the same source while a SC <0.90 indicates no correlation. SCs of identical, low silica glasses are likely to be lower than high silica glasses due to greater compositional heterogeneity. SC matrices were constructed to compare tephras within this data-set and with the results of other studies. Where previous studies have reported Fe as Fe₂O₃ this was converted to FeO for comparisons.

To investigate the general structure and internal correlations in the geochemical data, the southeast Alaska data-set was subjected to cluster analysis. Cluster analysis is a multidimensional technique for partitioning a data-set into discrete sub-sets, it has been previously used in tephra studies by King et al. (1982). A variety of techniques were tested including Single-Link, Complete-Link and Average-Link methods (Legendre & Legendre 1998). Results reported here were obtained by Average-Link clustering using a squared Euclidean Distance matrix. This method calculates the dissimilarity between clusters based on an average for each cluster (averages calculated using the Unweighted
Pair-Groups Method Average; UPGMA). Data were analysed in terms of both individual analyses and the averages of each data set, all major oxides were included in the analysis. Cluster analysis was carried out using SPSS v.10.
5.4 HUMIFICATION METHODS

Humification is the process of decomposition occurring in peatlands. More highly humified peats are more amorphous and darker in colour (Clymo 1983). The degree of humification varies with the moisture conditions at the mire surface. Biotic and physical decomposition processes are less effective in water-logged, anaerobic conditions, therefore the degree of humification depends in part on the time taken to reach the anaerobic layer. When the water-table is lower the time taken will be longer and the peat will be more humified (Aaby & Tauber 1975). As water tables in ombrotrophic mires are believed to be directly linked to climate, degree of humification can therefore be used as a proxy-climatic record.

Peat decomposition can be assessed using a variety of criteria. More humified peat is usually darker in colour, has fewer distinct macrofossils and a greater concentration of the complex organic acids which are the end products of decomposition. Several methods based on these properties have been used to assess humification, with varying degrees of success. Initial studies used visual inspection of peat colour and consistency as part of analyses of peat stratigraphy. Crude changes in peat humification (recurrence surfaces) were a key part of early peatland-palaeoclimate research including the Blytt-Sernander scheme (Blackford 1993). A refinement of qualitative description of peat was Von Post's ten-point scale, which applied a series of categories to try and achieve a degree of uniformity in description (Aaby 1986). These methods are largely subjective and are little used in modern studies but still have a role for the rapid description of long peat sequences (Nilssen & Vorren 1991, Robinson & Moore 1999). A semi-quantitative variant of this method is that used by Stoneman (1993) whereby the colour density of a peat solution is assessed by a method analogous to the secchi disk technique used in water quality studies. The accuracy of this method is however, questionable (Blackford & Chambers 1993). An alternative method of assessing peat humification is to consider the macrofossil remains in the peat. Levesque & Mathur (1979) investigated a number of variables that change with humification and found that the fibre content appears to be critical (Blackford & Chambers 1993). However, due to
differential decay rates of different plant species, there is a high possibility of including a
species signal in the data which may mask any true humification change. Therefore Blackford & Chambers (1993) suggested that a third method might be the most reliable.

The most widely used method of assessing peat humification is the alkali-extraction and colorimetry method (Overbeck 1947, Bahnson 1968; translated in Aaby & Tauber 1975). This method attempts to extract and measure the concentration of humic acids in peat. The concentration of humic acids in peat increases as peat decomposes and the plant matrix is broken down, allowing the potential to use humic acid concentration as an index of peat humification. Humic acids are generally extracted using sodium hydroxide and humic acid concentration assessed using colorimetry. It is assumed that because humic acids are dark brown in colour the less light which passes through a sample, the greater the humic acid concentration. Either transmission or absorption may be measured although transmission is more usual; a wavelength of either 540 or 550nm is used. Measured values may be converted to a ‘percentage humification’ value however this may not be entirely justified (Blackford & Chambers 1993). This method has been used in a large number of studies and appears to be robust and replicable (Aaby 1976, Blackford & Chambers 1991, 1995, Nilssen & Vorren 1991, Chambers et al. 1997, Mauquoy & Barber 1999, Chambers & Blackford 2001, Mauquoy et al. 2002, Langdon et al. 2003, Roos-Barraclough et al. 2004, Borgmark 2005).

Colorimetric humification analysis as a climatic proxy has the advantages of being relatively cheap, quick and simple when compared to other methods. The method is also more widely applicable than other proxy records as it works equally well in highly humified blanket mires (Chambers et al. 1997) and is unaffected by the problems of preservation which can be troublesome for other proxies. Humification analysis can reveal dry as well as wet phases in bog growth (Chambers & Blackford 2001). Humification analysis is particularly valuable in studies using multiple sites to allow identification of those sites with an optimal palaeo-climate record, or in long cores to choose which areas may be most interesting for more detailed work using alternative methods.
Problems and issues with the method

There are several problems with humification as a palaeoecological method. The most critical of these is uncertainty over exactly what the colorimetry method measures. Caseldine et al. (2000) have investigated the composition of NaOH peat extracts using their luminescence properties. Their results reveal that the organic acids extracted are primarily lower weight fulvic acids, amino acids and polysaccharides rather than the humic acids conventionally assumed. Of particular concern is the extent to which these substances may be extracted from differing plant species. While a species-signal is widely believed to have some effect on peat humification, the extent of this is unknown. The chemical processes governing both peat decomposition and the alkali extraction methodology are inadequately understood; this constitutes a serious cause for concern when using humification as a climatic proxy. However, humification results from numerous studies do show general agreement both between sites and with results of other methods (Baker et al. 1999, Charman et al. 2001, Gunnarson et al. 2003). It therefore seems that although the mechanisms remain uncertain, there is clearly some degree of direct or indirect climatic control on peat humification. Humification is still a valuable technique but results must be interpreted carefully and replication with other palaeoecological methods is desirable.

Role of the method in this study

In this study, humification analysis is one of the key palaeoecological techniques used. The major advantages of humification analysis is that it is applicable to all peat types including old and highly humified peat. Humification has been studied across most major tephra layers in this study and has produced useful data from locations for which testate amoebae and macrofossil analysis was not successful. Humification serves as a climatic proxy but it is also possible that it may also be affected by the direct impact of volcanic products. Sanger et al. (1994) have shown that DOC flux is acidity dependent, suggesting the possibility that leaching of organic acids may be increased in acidified peats. Furthermore, studies have suggested changes in the peat decomposition process in
acidified peats (Gorham et al. 1984, Sanger et al. 1994, 1996); it is possible that these changes could impact upon the humification of the peat. Humification, in combination with the other palaeoecological methods, may therefore help to establish whether there are any impacts upon these peatlands and the possible modes of these impacts. In addition, humification has been examined throughout the entire core from four sites in southeast Alaska to reconstruct the overall palaeo-hydrological record. This will allow the humification results across the tephras to be placed in a wider context.

**Practical methodology**

The methodology used in this study followed Blackford & Chambers (1993). Samples of peat were placed in crucibles and oven dried. The dried peat was ground to a fine powder with a pestle and mortar; large plant remains were cut into small pieces with a scalpel. A sub-sample of 0.1g (in most cases) of powdered peat was weighed to 4dp and placed in a 150ml conical flask. The remaining peat was weighed and combusted to calculate LOI. 50ml of freshly prepared 8% NaOH was added to the weighed sample and brought to the boil on a hot-plate, the temperature was lowered and samples heated for an hour. The samples were removed from the heat, allowed to cool and made up to 100ml with distilled water. The samples were filtered through Whatman 'Qualitative 1' filter paper and allowed to stand. After four hours from the initial mixing the samples were measured three times in a Spectrophotometer at 540nm and the average transmission value recorded. Readings were adjusted using the LOI values, to account for the inorganic component of the peat, particularly tephra.
5.5 TESTATE AMOEBAE METHODS

Several quantitative studies of testate amoebae ecology, including that described in this thesis, have shown that availability of water expressed as soil moisture or depth to water table (DWT) is a prime factor determining species composition (e.g. Charman & Warner 1992, 1997, Warner & Charman 1994, Woodland et al. 1998). In ombrotrophic peatlands, DWT changes are assumed to be directly related to climate. Testate amoebae allow the potential to quantitatively reconstruct DWT changes and therefore climate change.

Testate amoebae analysis has several advantages as a source of proxy-climate data. Testate amoebae species are found in peatlands around the world, many of the species are found globally and seem to have equivalent ecological preferences (Charman et al. 2000, Booth 2001, Finlay et al. 2001). Testate amoebae analysis therefore has widespread applicability as a climatic proxy and results may be comparable between regions. Testate amoebae show a strong preference for DWT conditions; most quantitative studies show DWT as the most important environmental variable. Many other organisms used in palaeoecological studies have more complicated environmental preferences and the variable of key interest may not be the most significant potentially undermining reconstructions. Perhaps the key advantage of testate amoebae analysis is the possibility of using transfer functions to allow quantification in terms of a real environmental variable. Results produced by these methods can therefore be compared with measured water table and meteorological records to allow interpretation of species changes in a rigorous statistical manner; this is not possible with other palaeoecological proxies (Charman & Hendon 2000, Charman et al. 2004, Schoning et al. 2005). Physical proxies such as peat humification analysis generally only show relative moisture changes and the ecology of other peatland organisms is generally too complicated to make a transfer function approach viable. There is the potential for reconstructions based on testate amoebae to be highly accurate, the study of Woodland et al. (1998) suggests that it may be possible to reconstruct DWT with an error of less than 4cm.
There are several potential problems with the application of testate-amoebae analysis in palaeoecology. Perhaps the most serious is the potential for differential preservation. It has been noted in many studies that some species that are abundant on the surface of peatlands are found rarely, if at all, in palaeoecological studies—this is illustrated particularly well by the *Euglypha* species which are rarely encountered in palaeoecological studies. The study of Lousier & Parkinson (1981) found differential preservation of tests in mineral soils with tests made up of plates decomposing more rapidly than those of particles (Tolonen 1986). In a peatland palaeoecology study Wilmshurst *et al.* (2003) demonstrated correlation between species diversity and humification which they took to suggest that tests may be broken down in more decomposed peats. Differential preservation of testate amoebae has also been demonstrated experimentally (Hendon & Charman 1997, G. Swindles, Queens University Belfast, personal communication) however these studies have used harsh chemical treatments, which would not be found naturally. Differential preservation is clearly a cause for concern in testate amoebae palaeoecology. Species loss may reduce the usefulness of reconstructions and potentially undermine quantitative studies. A further problem is the lack of modern analogues for some palaeo-testate communities. Where species are abundant in the palaeoecological record but absent from modern studies it may prove impossible to carry out quantitative reconstructions (Hendon 1998, Wilmshurst *et al.* 2003). A particularly notable instance is *Difflugia pulex*, a small *Difflugia* species that is highly abundant in some palaeoecological studies but virtually absent from modern transfer-function studies. These problems are awkward but perhaps inevitable given several thousand years of evolution, range change and competition. The specific reasons for the apparent decline of some species are uncertain.

A persistent problem with testate amoebae analysis is the lack of a definitive taxonomy. This has lead to significant taxonomic differences between authors that may impair cross-comparison of results between studies and the use of transfer functions. This problem has been approached by grouping species that are difficult to differentiate. However Bobrov *et al.* (1999) showed that such an approach may lead to loss of
ecological information. A related problem is the possibility of intra-specific variation in morphology. This may impair interpretations particularly as morphology may be influenced by environmental conditions (Heal 1963, Charman 1999, Booth 2001). A particular issue with testate amoebae-climate reconstruction is the marked preference of testates for Sphagnum-dominated sites. Many peatlands, which might otherwise produce usable proxy-records, are inhibited by the absence of Sphagnum domination through part or all of the core leading to absence of testates or vastly reduced species abundances (Charman et al. 2001, Wilmshurst et al. 2003). This may therefore be a factor limiting the applicability of the method in many mires of the world.

A final distinct problem with the methodology is the methods used for preparing samples. In initial studies, testate amoebae were often counted along with pollen (Aaby 1976, Barber 1981). These studies met with variable success as up to 80% of tests may be destroyed by pollen preparations (Hendon & Charman 1997). More recent studies have used water-based methods (Tolonen 1986, Hendon & Charman 1997). While these preparations may not destroy tests there are still problems with preserving slides and with the lack of maneuverability of tests on the slide (Charman 1999).

There are several important problems with testate amoebae analysis, however these are not insurmountable. Although species may be lost from the palaeoecological record the majority of species are not and those species which are most abundant in modern studies are also usually most abundant in palaeoecological studies. The issue of taxonomy is less critical if the same scheme is strictly applied to both modern (transfer function) studies and palaeoecology. Water-based preparation methods have largely removed the issue of test destruction and the issue of test maneuverability on the slide is not critical as long as a consistent taxonomy is adopted.

Holocene climate reconstructions using testate amoebae show a high degree of similarity between sites, with the results of other proxies, with meteorological records and with climatic indices (Charman et al. 1999, 2001, 2004, Charman & Hendon 2000, Charman 2001, Hendon et al. 2001, Schoning et al. 2005). The ability of testate amoebae analysis to produce quantitative reconstructions of DWT makes it perhaps the most useful technique for peatland palaeoclimatology. Although there are several persistent problems with varying aspects of the technique, the method does appear essentially sound.
Role of the method in this study

In this study testate amoebae analysis is used as part of a range of techniques to investigate direct or indirect volcanic impacts on peatlands. Testate amoebae have been used as indicator species in monitoring anthropogenic impacts on peatlands (e.g. Davis & Wilkinson 2004) and can be expected to respond to volcanic forced changes. Specifically, testate amoebae are heavily affected by both DWT and pH, both of which may be changed by volcanic impacts. DWT may be altered by a volcanic induced climatic change or conceivably by an impact on mire hydrology. pH may be altered by an input of volcanic acidity or through an impact on peatland plants. Testate amoebae analysis may therefore help to both reveal any volcanic impacts and to investigate the modes of these impacts.

Practical Methodology

Sample preparation was based on the method of Hendon & Charman (1997). Peat sub-samples of approximately 1 cm³ were placed in a 100ml flask with 50ml of water. Samples were boiled for approximately ten minutes to disaggregate the peat and release the tests. The solution was initially sieved at 300μm to remove the coarse fraction and then back-filtered at 15μm to remove fine, highly degraded organic particles. The resulting material was centrifuged at 3000RPM for five minutes to concentrate the tests. Prepared samples were stored in distilled water in 5ml glass vials. Slides were prepared by mixing a drop of the sample with glycerol and were examined microscopically at 400x magnification. Tests were identified and counted with reference to the existing body of literature (including Deflandre 1929, 1936, Grospietsch 1964, Ogden & Hedley 1980, Ogden 1983, Luftenegger et al. 1988, Beyens & Chardez 1995, Charman et al. 2000, Clarke 2003). The taxonomic scheme used was broadly the same as in the transfer function study. Some species were initially sub-divided (as shown in testate amoebae diagrams) but have been grouped for quantitative interpretation. The test-forming bdelloid rotifer Habrotrocha angusticollis was also counted and included in percentage
calculations. Results were quantitatively interpreted in terms of pH and DWT using the WA-PLS transfer functions. Boot-strapped error estimates were calculated for each sample using 1000 cycles.
5.6 MACROFOSSIL METHODS

The majority of peat consists of sub-fossil plant remains. As such, plant macrofossils have been studied for as long as peat stratigraphy itself. In ombrotrophic peatlands, this plant material may undergo comparatively little decomposition once it passes from the acrotelm into the catotelm and may still be identified to species level after thousands of years (Janssens 1983). Peatland plant species have different tolerances for environmental variables including depth to water table (DWT). By looking at species changes within a peat section it may be possible to infer changes in water table depths, which can be used as a proxy for climatic changes. *Sphagnum* species (particularly sections Cuspidata and Subsecunda) are taken as indicating wet conditions, while monocotyledons and Ericales, indicate drier conditions and *Racomitrium lanuginosum* and unidentified organic matter (UOM) indicate driest conditions (Tallis 1995, Blackford 2000). The majority of studies have interpreted results qualitatively by reference to the known autecology of the species.

Several recent studies have used the 'quadrat and leaf counts' (QLQ) method of Barber *et al.* (1994) for macrofossil analysis. This methodology uses a two-stage procedure. Initially, samples are examined under a low-power microscope and the abundance of the major components estimated using a grid graticule. Following this a sub-sample of *Sphagnum* leaves are picked out and identified to section or species level under high power microscopy. Results of studies using this methodology show consistency between sites and with other palaeoecological methods from peatlands (Stoneman 1993, Barber *et al.* 1998, Mauquoy & Barber 1999a).

Problems and issues with the method

There are several important issues with using macrofossil analysis as a palaeoclimatic proxy. One of the most significant of these is the difficulty in interpreting macrofossil results in terms of climatic change. The distribution of peatland plants is controlled by a variety of environmental factors including nutrient status, hydrology and climate. These ecological controls are more complex than for other organisms such as
testate amoebae. The transfer function approach which has been used successfully in other areas of palaeoecology has not been widely applied to peatland plants due to the complexity of these relationships (Birks et al. 1998). Recent studies have used axis-1 scores from unconstrained ordination to summarize macrofossil data in a single series, results interpreted using this methodology show a high degree of correlation with climatic records (Barber et al. 1994).

A further cause for concern when using macrofossil analysis is the extent to which different species are preserved in the macrofossil record. It has been often noted that some species found in abundance on peatlands are not found in the palaeoecological record; perhaps most graphic is the absence of lichen species from palaeoecological studies. This selective decay means that potentially useful information is lost and ecological interpretations are complicated. Problems are also posed in some sites where, the peat is too decomposed to allow the identification of any macrofossils for all or part of the profile (Blackford 2000). A problem with many biological proxies including macrofossil analysis is the possibility for species composition changes due to competition effects rather than any environmental change. In the United Kingdom several studies have investigated the decline in Sphagnum imbricatum over recent centuries. It is unclear if this is associated with any climatic change or is a species-competition effect (Stoneman et al. 1993, Mauquoy & Barber 1999b).

A further problem with the method is the speed of response. The vegetation of a peatland subject to a rapid climate change will not change simultaneously. Instead, those species adapted to the changed conditions will expand their distributions and those less adapted will contract. At a single sampling spot this could result in a lag followed by a rapid species change some time after the onset of the event. There is also uncertainty over how sensitive the macrofossil record is to small changes. For this reason, choice of sampling spot in a climatically sensitive location (usually a lawn microform) is particularly critical to macrofossil studies. Overall, there is reasonable evidence that the macrofossil record does provide a record of climatic change however the sensitivity of this record is open to question.
Role in this study

In this study a basic macrofossil analysis is undertaken to identify the major peat components and any gross changes in peat composition. Peat components are classified into five broad groups but not identified to species level. Macrofossil analysis may identify any volcanic impacts on the plants growing on the mire and provide further information on the direct and indirect impact of volcanic products on these peatlands. Macrofossil analysis supports humification and testate amoebae analysis in determining the scale of any effects. A more rigorous methodology was not adopted as it was considered that macrofossil analysis was likely to be less sensitive to short-term volcanic induced changes than the other palaeoecological methods used.

Practical Methodology

In this study a basic macrofossil analysis was undertaken based on the first stage of the QLC method of Barber et al. (1994). A sub-sample of peat was boiled in distilled water and broken up into a 300μm sieve. The sub-300μm component was used in testate amoebae preparations and the larger fraction for macrofossil analysis. The fraction over 300μm was further cleaned using a jet of tap water until no visible particles were released; the cleaned sample was stored in tap water in a universal tube. A sub-sample was poured into a cleaned petri dish and distilled water added to give a mono-layer of macrofossil remains. The samples were examined under a low-power microscope at 50x magnification. A sheet of graph paper was placed under the sample to give a visible grid of squares (akin to the grid graticule used in previous studies). Peat components visible under the microscope were divided into five categories:

1) *Sphagnum*. Including all recognizable *Sphagnum* leaves and stems and other bryophyte material.
2) Monocotyledons. Including all monocotyledon (sedges, grasses, rushes) remains, including rootlets.
3) Ericales. Including all remains from Ericaceae, other shrubs and woody plants including trees.
4) UOM. Unidentifiable Organic Matter. Small particles of highly decomposed and unidentifiable material.

5) Other. Material which is not easily assigned to other classes. In particular this category includes recognizable seeds and insect remains.

The number of grid squares (out of 100) in which any of these components occurred was counted from four locations for each sample. For each quadrat the abundance of each component was calculated as a percentage of the sum total of all the components. For each sample an average was calculated from the results of all four quadrats.

Palaeoecological methods - a summary

Three palaeoecological methods have been applied in this study - humification, testate amoebae and macrofossil analysis. Such a multiproxy approach allows the potential to gain a better understanding of any impacts and to separate out non-volcanic variability. While all three methods are sensitive to hydrological change they all may respond to different aspects of a direct volcanic impacts. Macrofossil analysis may reveal impacts on surface vegetation, while testate amoebae are sensitive to changes in poor water chemistry and humification may reveal any impacts on the peat matrix itself. Therefore by comparison of the three proxies it may be possible to gain an understanding of the processes occurring.
5.7 RADIOCARBON DATING

A chronological framework allows both the tephra layers and their impacts to be dated. It is possible to date tephra layers directly by radiometric methods including fission-track and K-Ar dating. These techniques have the advantages of dating the tephra itself rather than the sedimentary context but have very large associated errors (Naeser et al. 1981); an alternative method is therefore needed. Several radiometric and other dating methods have been used for dating peat including $^{210}$Pb and $^{241}$Am isotopes (Oldfield et al. 1995), spheroidal carbonaceous particles (SCPs; Rose et al. 1995), moss increments (Belyea & Warner 1996), pollen and geochemical markers (Turetsky et al. 2004). These methods all have their advantages but are mostly limited to very recent sediments. The most valuable and widely used dating technique for peatland palaeoecology is radiocarbon dating. Radiocarbon provides the main chronological framework for this study.

Radiocarbon ($^{14}$C) is a naturally occurring radioisotope produced in the atmosphere by the displacement of protons from nitrogen atoms (Libby 1955). Once formed $^{14}$C decays to form $^{14}$N at a constant rate with a half-life of 5570±30. $^{14}$C is continually taken up by organisms and stored within their tissues. While an organism is alive, $^{14}$C is maintained in equilibrium with the atmosphere, however after death no new $^{14}$C is added and the activity begins to decrease. This decay is constant over time; it is therefore theoretically possible to use the remaining $^{14}$C activity to calculate the time of death (Pilcher 1991). $^{14}$C activity can be measured in two ways. Conventional (radiometric) techniques involve the detection and counting of β particles emitted from a sample over time. As $^{14}$C concentration is low, a large sample is required to detect a reasonable number of β particles. Accelerator mass spectrometry (AMS) techniques use particle accelerators as ultra-sensitive mass spectrometers to count the actual number of $^{14}$C atoms in a sample. This method allows the use of smaller samples (a few mg of C) and is more rapid than radiometric methods (Naeser et al. 1981).
Problems and with the method

One of the key issues in radiocarbon dating is the temporal variability of atmospheric $^{14}$C. $^{14}$C levels fluctuate over time, primarily due to variability in solar activity. This means that radiocarbon dates, expressed in conventional terms, do not match a calendrical age. $^{14}$C variation has been reconstructed through the Holocene by dating tree-ring material of known age (Stuiver & Pearson 1986). The curves produced allow the potential to calibrate a radiocarbon date in calendar years. However problems arise because of the 'wiggles' in the calibration curve. This means that a radiocarbon age may produce multiple intercepts on the calibration curve giving a variety of possible calendrical dates. For instance, for a radiocarbon date of 9.6±100 ka BP there are a total of seven possible calendrical ages, which means that a 2σ calibrated age range spans over 1ka (Lowe & Walker 1997). Additional problems arise due to the presence of plateaux on the calibration curve, meaning that samples across a span of radiocarbon ages produce very similar calendrical dates.

The wiggles in the radiocarbon calibration curve present an opportunity as well as a challenge to the use of radiocarbon for dating. It has been shown that by obtaining a sequence of very closely spaced radiocarbon dates it is possible to produce a 'wiggle' which can be matched up with a corresponding 'wiggle' in the calibration curve. This technique, known as wiggle-match dating (WMD) has the potential to produce exceptionally accurate dates (van Geel & Mook 1989). The method has gained increasing use in high-resolution dating of peatlands (Kilian et al. 1995, Mauquoy et al. 2002).

All radiocarbon methods are particularly limited in several respects. Radiocarbon dating is a time consuming and expensive process. Improved techniques such as AMS and new methodologies such as wiggle-matching have only increased these constraints. For this reason, most studies have only used a limited number of dates, limiting the accuracy of the resulting age-depth model and therefore the results. Radiocarbon dating is also limited by the volume of material required, AMS dates can be carried out on samples with only a few mg carbon however this can still be a problem in some studies (although this is rarely the case with peat samples). A concern when dating some organic materials is that dates are systematically too old or too young, such a reservoir effect has been
noted with peat samples (Kilian et al. 1995, although see contrary results in Blaauw et al. 2004). The practical problems inherent in radiocarbon dating are illustrated by the spread of results shown in inter-laboratory comparison exercises (e.g. Currie & Pollach 1980). Even at its most refined, radiocarbon dates only represent estimates and their associated errors. Radiocarbon cannot achieve the precision which dendrochronology and varve chronologies are capable of.

Radiocarbon dating tephra layers

Radiocarbon has been widely used in dating tephra layers. In areas very close to the volcanic source problems have been encountered due to anomalous radiocarbon concentrations produced by volcanic gases (Calderoni & Turi 1998, Pasquier-Cardin et al. 1999). In distal regions this has not been a problem and tephra layers have been routinely dated in peatlands. Dugmore et al. (1995b) outlined three approaches which may be adopted. The most widely used approach is simply a single date across a tephra in one site. While this is simple and inexpensive it will only give a poor-age estimate and aberrant dates will not be detected. For distal tephras, samples can usually be taken which span the tephra, for proximal tephras this is usually more complicated due to the possible disruption of peat growth by tephra deposition. In these cases, samples are usually taken from directly below the tephra as there may be a time lag between tephra-deposition and renewed peat growth above the layer (Dugmore et al. 1995b). An alternative approach is to combine radiocarbon dates from the same tephra in multiple sites. This methodology allows the dating precision to be improved and any outlier dates and site-specific effects to be eliminated; further information may be obtained by interpreting results within a Bayesian framework (Buck et al. 2003). The final, frequently used approach is to use multiples date across one tephra including a wiggle-matching approach. This method has the advantage of potentially producing a highly accurate date although there are potential problems due to site-specific effects and accumulation rate changes associated with tephra deposition (Dugmore et al. 1995b). This method has been used to produce high precision dates in several recent studies (Pilcher et al. 1994, 1995, Birks et al. 1996, Okuno & Nakamura 2003, Plunkett et al. 2004). Both of the two latter methods are
valuable techniques; arguably the most reliable approach is by using multiple sites, however many studies do not have the luxury of finding the same tephra in numerous sites.

Role of the method in this study

In this study, radiocarbon dating fulfils several key roles. Radiocarbon dates of tephra layers may aid identification of tephras for which EPMA is not available or is not diagnostic. By comparison with volcanic chronologies and taking consideration of the likely size of the eruptions it should be possible to use radiocarbon dating of tephra layers to help identify them. By allowing identification of probable source eruptions, radiocarbon dates may allow judgements to be made about whether any impacts seen in the palaeoecological record are likely to be direct or indirect (climatic) impacts given the scale of the eruption. Radiocarbon dates could also enable the dating of these eruptions to be improved and their impacts to be investigated by looking at other historical, palaeoecological and palaeoclimatic records. Multiple radiocarbon dates across individual tephra layers could allow the longevity of any impacts upon the peatland to be investigated. This is of value to allow judgements about the scale of the impact and may also aid in separating direct from indirect volcanic impacts. Finally, by having several radiocarbon dates from each core, it is possible to build an age-depth model for the site. This is of value to aid identification of tephra layers which have not been directly dated, to investigate the longevity of impact of tephra layers and to look at the full-core palaeoecological record.

To fulfill these requirements, multiple radiocarbon dates were required. To build preliminary full-core age-depth models and aid tephra dating; seven ‘rangefinder’ dates were obtained from the five sites in southeast Alaska. To aid tephra identification, three of the major tephra layers in southeast Alaska were dated using individual radiocarbon dates. For the Sterling site in South-central Alaska a dates was obtained across the lowermost tephra to both aid its identification and construct an outline age-depth model.
Practical Methodology

Great care was taken to avoid contamination in sample preparation for radiocarbon analysis. Samples were taken from the peat cores using cleaned instruments whilst wearing gloves. Samples were removed from the centre of the cores to minimize the risk of contamination by 'modern' carbon. For the initial seven 'rangefinder' dates from southeast Alaska, bulk samples were used. Samples of approximately 1 cm$^3$ were extracted from the cores, placed in clean plastic bags and submitted to the radiocarbon laboratory.

For the radiocarbon dates of tephra layers, a greater degree of precision is required. Homogeneous macrofossils were extracted and used for dating. Previous radiocarbon studies in Alaska have shown that larger macrofossils are generally more reliable for dating (Nelson et al. 1988). Macrofossils were picked and cleaned following the 'ACCROTELM' protocol described by Mauquoy et al. (2003). Bulk samples (~2 cm$^3$) were broken up into a 300 μm sieve. At least 11 of distilled water was passed through the sieve to remove most of the fine material. The coarse fraction was stored in distilled water in clean universal tubes. For macrofossil picking, a sub-sample was placed in a clean petri dish with distilled water. Samples were examined under low-power microscopy at 50X magnification. Individual macrofossils were carefully picked out using tweezers or a Pasteur pipette. Where available, Sphagnum leaves and stems were selected. Sphagnum materials have been widely used in high-resolution radiocarbon studies and appear to have minimal problems with contamination. When Sphagnum was not present in sufficient quantities monocotyledon remains were used. Where possible, homogeneous, large and intact leaf sections were chosen (mostly Eriophorum spp.). All selected macrofossils were placed in a second clean petri dish. These samples were inspected under the microscope for any signs of contamination. Selected macrofossils were transferred to a clean 20 ml glass bottle with distilled water. 10% HCl was added to the samples and left overnight, the supernatant was poured off and the samples were topped up with distilled water and this repeated until the pH of the solution was near neutral. Finally, the samples were again inspected for any contamination that may have
entered during cleaning, placed in 5ml glass vials and dispatched to the radiocarbon laboratory.

Radiocarbon dating was carried out at two different radiocarbon laboratories. Rangefinder AMS dating and three AMS dates from tephra in southeast Alaska were carried out at the NERC radiocarbon laboratory, East Kilbride, Scotland (SUERC prefix). Radiometric dating from the Dot Lake B and Sterling sites were carried out at the Ukrainian Research Centre for Radiation Medicine, Kiev, Ukraine (URCRM prefix). Radiocarbon dates were calibrated using the program OxCal v.3.10 (Bronk Ramsey 2005). Full details of radiocarbon datings are given in the Results section.
5.8 STATISTICAL ANALYSIS

Most previous studies of tephra impacts in the palaeoecological record have assessed impacts by qualitative inspection of the data. This is an inherently subjective procedure. In this study I attempt to statistically investigate any impacts occurring. I use two general approaches: zonation analyses and partial RDA. Both of these techniques are applied to the testate amoebae data to detect any change associated with tephra deposition.

5.8.1 Zonation analyses

Zonation analyses are widely used in palaeoecology for sub-dividing biostratigraphical diagrams facilitating description and interpretation of the diagram and allowing correlation between sites (Gordon & Birks 1972, Birks & Gordon 1985). In this study, zonation analyses are used to examine if there is a difference between testate amoebae communities pre- and post-tephra deposition. If a single zone boundary coincides with the location of the tephra layer, this provides circumstantial support for a volcanic impact upon the system.

Techniques fall into two groups: agglomerative methods, which work by successively grouping similar samples and divisive techniques, which successively split the overall sequence. Agglomerative methods are based on conventional cluster analysis techniques with the constraint that the clusters must be composed of samples in stratigraphic order. Two agglomerative techniques are tested here: constrained incremental sum of squares (CONISS) and constrained single link clustering (CONSLINK). CONSLINK is an agglomerative clustering method where samples are added to a group based on their similarity to any single sample in that group. The application of the method has been limited due to the problem of ‘chaining’, i.e. that with the increasing size of a group it is increasingly probable that the group will contain a member similar to an unassigned sample (Gordon & Birks 1972). A particular problem with the application of CONSLINK in this study is that the method may show several
potential splits at the same point in the hierarchy making it impossible to determine the single most important split in the data set.

Constrained incremental sum of squares (CONISS) is an agglomerative hierarchical method which groups samples and assigns zone boundaries so as to minimize within-zone dispersion assessed by sum of squares (Grimm 1987). CONISS is perhaps the most widely applied technique for zoning biostratigraphic diagrams as it produces a sequence of similarly sized zones, which often agree well with qualitative zonation. However, CONISS has also been shown to assign a sequence of similarly sized zones to randomized data. A general problem with all of these agglomerative methods is difficulties when assigning zone boundaries to gradual changes (Bennett 1996).

An alternative approach to zoning biostratigraphic sequences is by divisive methods. These techniques consider the whole data-set and the reduction in overall variance which may be achieved by the insertion of zone boundaries. As such the methodology is more focused on the sequence as a whole unlike the agglomerative methodology, which is more focused on the samples. Two variants of this divisive methodology are examined with variance assessed by information content (SPLITINF) or sum of squares (SPLITLSQ; Gordon & Birks 1972, Birks & Gordon 1985). These methods can outperform agglomerative methods, particularly at detecting small but stratigraphically consistent changes over several levels (Gordon & Birks 1972). The SPLITINF and SPLITLSQ techniques are binary approaches which first split the overall data-set in two and then successively split these zones into smaller sub-divisions. An alternative approach is optimal partitioning, this a non-hierarchical approach which starts afresh for each number of zones to reduce the overall variance in the data-set (Bennett 1996). In this study, it is only the first division that is of interest so the advantages of optimal partitioning are unimportant and the technique has not been used.

All testate amoebae data-sets were zoned using each of the four methods (CONSLINK, CONISS, SPLITLSQ and SPLITINF). Zoning was carried out on the full data including rare species and with no data transformation (Bennett 1996). All zonation analyses were carried out using the program ZONE v.1.2 (Juggins 1992).
5.8.2 Redundancy analyses

Zonation analyses are useful to assess whether there is change coincident with the tephra layers, however it is a relatively crude approach and cannot assess whether this change is either statistically significant or consistent with a volcanic impact. An alternative approach is to use constrained ordination with an explanatory variable designed to simulate a volcanic impact. This approach has been previously applied in palaeoecological studies of volcanic impacts on lakes (Lotter & Birks 1993, Barker et al. 2000, Eastwood et al. 2002).

Previous studies have taken two distinct approaches to modelling volcanic impacts. In the initial research by Lotter & Birks (1993) tephra concentration was not enumerated. The response to a volcanic impact was simulated as an exponential decay process from an arbitrarily defined value of 100 at the tephra layer. More recent studies (Barker et al. 2000, Eastwood et al. 2002) have calculated tephra concentrations and used these as the explanatory variable. Variance partitioning exercises were carried out to eliminate the effects of non-volcanic variables such as climate and lithology.

In this study (partial) redundancy analysis (RDA) the constrained form of principal components analysis (PCA) was used to investigate volcanic impacts on the testate amoebae data and variance partitioning carried out to separate volcanic from non-volcanic variability. This technique was selected as preliminary detrended correspondence analyses (DCA) showed the gradient lengths to be short (<1.4 standard deviations); therefore ordination based on a unimodal species response (i.e. Canonical Correspondence Analysis: CCA) is not necessary. As the testate amoebae data is based on percentages it was log_{10}-transformed prior to analysis, the data sets were double centered by species and samples. Monte Carlo tests were used to provide a test of the null hypothesis that the species and explanatory data are unrelated and to provide an estimate of the significance level of any relationships. 999 Monte Carlo permutations were used.

Four explanatory variables were used: depth, macrofossil data, humification and a model of volcanic impact. The variable 'Volcanic' consists of two components: an exponential decay model and a simple before (0) and after (1) nominal variable. The exponential decay function is identical to that used by Lotter & Birks (1993) and is
defined as $\exp(-\alpha t)$ where $\alpha$ is the decay constant, given a value of 0.5 and $t$ is sample time (i.e. depth) after the tephra peak. This variable is assigned a value of 0 prior to the tephra peak and then a value of 100 at the tephra peak sample. This structure is considered more appropriate than simply using tephra concentration profiles as these are primarily a function of the post-depositional movement of tephra through the peat profile and are not related to volcanic impacts. This model assumes that the impact of a volcanic event will be represented as a large impact at the time of tephra deposition and will decrease with time. This seems a reasonable assumption regardless of what mechanism an impact may occur by. For the ST 24 data the major tephra peak was taken to be the lower of the two LOI troughs. For the MP 27 data the missing sample containing the tephra peak was excluded from the analysis and the tephra peak taken to be the sample directly above.

Humification and macrofossils, the two other proxy-records were also included in the variance partitioning analyses. It is possible that both of these variables may have an indirect impact on testate amoebae data through testate amoebae vegetation preferences (macrofossils) and test decomposition processes (humification). Therefore to identify any independent volcanic impact on testate amoebae it is necessary to eliminate these effects. Humification data was averaged to reduce the resolution to that used in the other analyses, where necessary. Macrofossils were included as all five counted peat components. Samples in which either macrofossil or humification data were not available were excluded from the analysis. Depth was also included in the variance partitioning exercise as a surrogate for time. This has been carried out in previous studies and allows the potential to separate out the effect of pre-existing environmental change, in this study primarily long-term climatic change. Variance partitioning was carried out to investigate volcanic impacts with and without the contribution of the other palaeoecological proxies and depth and the independent contribution of each of the proxy-records.
CHAPTER 6. PALAEOENVIRONMENTAL RESULTS

6.1 TEPHRA RESULTS

Tephra layers were located in many of the cores. Layers are named by their site code and depth in cm, therefore for instance the SPM 26 tephra reaches a peak concentration at 26 cm in the Spaulding Meadows site. The tephras are named by the depth at which they were originally noted, for the Kenai tephras a different core was used in the palaeoecological analyses from the initial tephra study and therefore the depths do not all exactly agree. Tephras are described below according to their appearance, concentration and geochemistry.

6.1.1 Southeast Alaska

A total of fourteen tephra layers were located in these sites. A maximum of four layers in a single site indicates there are at least this number of separate tephras (Fig. 6.1.1, see also Payne & Blackford 2004). All tephras found in southeast Alaska are non-visible micro-tephras. Tephras are all relatively silicic in composition (72-79%); EPMA data are shown in Table 6.1.1. The tephras are described below.

SPM 26. This micro-tephra layer is substantial in size (maximum concentration c.1.7x10^6 shards/gram dw.) and is mostly made up of shards between 50 and 75μm in size. The EPMA data show that the tephra is moderately silicic, and has values for most major oxides towards the middle of the range for the southeast Alaska sites. It is notable for a relatively low average sodium concentration. The tephra is similar in composition to several others including LNA 39, ECR 32, MTR 146 and CHP 184.

ECR 32. This layer is relatively extensive (maximum concentration c.1.9x10^6 shards/gram dw.) and is composed of shards of varying size. A qualitative examination of the EPMA data show that this tephra is quite similar to many others, the highest degree of similarity is with LNA 39, SPM 26, MTR 146, LNA 100 and CHP 184.
and radiocarbon dates (dotted lines, the age shown is the mid-point of the calibrated age range).
LNA 39. This tephra is the second most extensive of the southeast Alaskan tephras (maximum concentration c.2.9x10^6 shards/gram dw.) and is composed of small shards. It is similar in composition to many other layers including ECR 32, SPM 26, MTR 146, LNA 100 and CHP 184. The data show a CaO content greater than many of the other tephras (Table 6.1.1).

LNA 100. This tephra is the most extensive of all the southeast layers (maximum concentration c.6.7x10^6 shards/gram dw.). It is similar in composition to many of the other tephras including MTR 146, ECR 32 and particularly LNA 39. It is notable for having the highest CaO content and a relatively high Na_2O content.

MTR 190. This tephra is one of the smaller layers (maximum concentration c.2.7x10^4 shards/gram dw.) composed of shards under 50μm in size. Only two shards were analyzed by EPMA but the composition appears to be distinct. The tephra is one of the most silicic, the averaged values show it to have low TiO_2, FeO, MgO and CaO contents compared to the other tephras. On the basis of this limited data it appears to bear little resemblance to any of the other southeast layers.

CHP 184. This tephra is one of the larger layers (maximum concentration c.2.2x10^6 shards/gram dw.) mostly composed of larger shards. It is similar in composition to several of the other tephras including ECR 32, SPM 26, MTR 146, and LNA 39. The tephra has one of the lowest FeO contents of these tephras.

ECR 100. This tephra is an intermediate sized layer (maximum concentration c.5.1 x10^4 shards/gram dw.) of relatively small shards. Only two EPMA analyses were possible but the tephra appears to have distinctive composition. The shards are highly silicic, have high TiO_2, low K_2O and low Al_2O_3. It bears only limited similarity to most of the other southeast tephras.
### Palaeoenvironmental Results

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<th>LNA 100</th>
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<th>ECR 32</th>
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*Table 6.1.1: Electron microprobe data for southwestern Australian rocks. Results are raw percentages from Bergen (B) and Edinburgh (E).*
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<th>Palaeoenviromnental Results</th>
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<td>MTR 190</td>
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ECR 162. This tephra is of limited extent (maximum concentration c.2.2x10^4 shards/gram dw.) and is composed of shards under 50μm. The layer has a distinctive composition noted by high TiO₂, very high FeO, high NaO₂ and relatively high MnO and MgO compared to other southeast tephras. It clearly does not correlate with any of the other southeast Alaska tephras with EPMA data.

MTR 146. This tephra is one of the smaller layers (maximum concentration c.1.6x10^4 shards/gram dw.) composed of larger shards. The tephra is similar in composition to several of the other layers including SPM 26, LNA 39, CHP 184, ECR 32 and LNA 100.

LNA 136. This tephra is a relatively small layer (maximum concentration c.2.7x10^4 shards/gram dw.) of fine shards mostly under 50μm. This region of the core was damaged during transit, no EPMA data were obtained.

LNA 465. This tephra layer is the sparsest layer detected (maximum concentration c.8.9x10^3 shards/gram dw.) representing just a few small shards. No EPMA data were obtained.

MTR 32. This tephra layer is relatively sparse (maximum concentration c.2.6x10^4 shards/gram dw.) and is composed of relatively small shards (mostly 25-50μm). No EPMA data were obtained. Given the similarity in depth to the CHP 33 tephra in the closest other site it is thought likely to be correlative. Both of these layers may well correlate with the ECR 32, LNA 39 and SPM 26 tephras.

CHP 33. This tephra is a substantial layer (c.6.6x10^5 shards/gram dw.) of mixed sized shards. No EPMA data were obtained but depth suggests correlation with MTR 32 and possibly ECR 32, LNA 39 and SPM 26 tephras.

SPM ~126. A tephra layer was found around this depth. However, the core was damaged in transit and no more detailed work was carried out.
TABLE 1.2: Electron microprobe data for SouthCentral Alaska epsilon. Results are raw percentages from Bergan (b) and Durnford.

### Palaeoenvironmental Results

<table>
<thead>
<tr>
<th>Mineral</th>
<th>ST 12</th>
<th>ST 24</th>
<th>ST 36</th>
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<tr>
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<tr>
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<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Mg 0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Fe 0.1</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Ca 0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Na 0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
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<td>0.1</td>
<td>0.1</td>
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<tr>
<td>K 0.1</td>
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<tr>
<td>Ti 0.1</td>
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(continued...)

(e) microprobe's also showing zetates of low and normal and calcite and carbon dioxide.
Palaeoenvironmental Results

<table>
<thead>
<tr>
<th>Site</th>
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<th>MP10</th>
<th>STE8</th>
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<td>2</td>
<td>3</td>
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<tr>
<td>Data</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Palaeoenvironmental Results

- Site MP27
- Site MP10
- Site STE8

## Layer Details
- Layer 1
- Layer 2
- Layer 3

## Data
- Various measurements and observations are recorded in the table.

---

Page 159
<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Depth (m)</th>
<th>Age (ka)</th>
<th>Palaeoenvironmental Results</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Site 1</td>
<td>0.5</td>
<td>10,000</td>
<td>Desert conditions</td>
</tr>
<tr>
<td>SK2</td>
<td>Site 2</td>
<td>1.0</td>
<td>8,000</td>
<td>Wetland conditions</td>
</tr>
<tr>
<td>SK3</td>
<td>Site 3</td>
<td>1.5</td>
<td>6,000</td>
<td>Forest conditions</td>
</tr>
<tr>
<td>SK4</td>
<td>Site 4</td>
<td>2.0</td>
<td>4,000</td>
<td>Wetland conditions</td>
</tr>
</tbody>
</table>

**MP39**

Palaeoenvironmental Results

- Desert conditions
- Wetland conditions
- Forest conditions
6.1.2 South-central Alaska

In south-central Alaska three visible tephra layers were found in the Moose Pass site and four in the Sterling site. The geochemistry of the south-central Alaska tephras is considerably more variable with many layers having a heterogeneous composition. This makes it relatively complicated to determine correlations. EPMA data are shown in Table 6.1.2.

ST 12. This tephra is a 2mm thick layer of fine pumice particles and glass shards. The particle size analysis shows two distinct peaks at c. 45 and 180μm (Fig. 6.1.2). The tephra is highly silicic and is notable for a low average Al₂O₃ content.

ST 24. This tephra is composed of fine glass shards and coarser pumiceus particles and spans 5mm. The particle size analysis shows two peaks at c.35 and 490μm (Fig. 6.1.2). The tephra is highly silicic and is characterized by low average Al₂O₃ and FeO.

ST 36. This tephra is an 4mm thick layer of glass shards and fine pumiceous particles. The particle size analysis shows twin peaks at c.35 and 175μm (Fig.6.1.2). The tephra is silicic and is notable for low average Na₂O and K₂O contents.

ST 68. This deposit is a 3mm thick layer of silicic tephra shards. Particle size analysis shows two peaks at c.40 and 215μm (Fig. 6.1.2). The geochemical data show the tephra has low average FeO and TiO₂.

MP 10. This tephra is a 10mm zone of mixed sized particles. Particle size analysis shows peaks at 30 and 450μm (Fig. 6.1.2). The EPMA data shows the tephra has two distinct populations. Population MP 10a is more silicic (over 73% SiO₂ normalized) than population MP 10b (under 71% SiO₂). The MP 10a layer has notably low MgO and CaO. The MP 10b population is distinct from the silicic populations described previously particularly in terms of a high FeO, MgO, and CaO content. The MP 10a population
Fig. 6.1.2 South-central Alaska tephra particle size
bears a degree of similarity to the ST 24 tephra and a lesser degree of similarity to ST 12. This layer is similar in particle size to ST 24 (Fig. 6.1.2).

MP 27. This tephra is a 7mm thick layer of glass shards. This is the only layer from south-central Alaska with a monomodal particle size distribution showing a peak at c.65μm (Fig. 6.1.2). The EPMA data for this layer is relatively homogeneous with the exception of a single shard analysis. This analysis is sufficiently different to justify terming it a different population (MP 27a). This shard is moderately silicic with notably low CaO content. The major population (MP 27b) has the lowest average silica content of all tephra layers examined (59.7%) and extremely high Al₂O₃, FeO, CaO and MgO and low K₂O. This population is qualitatively similar to the MP 39 layer.

MP 39. This layer has a mixed size distribution and is 4mm thick. The particle size analysis shows peaks at 60 and 175μm (Fig. 6.1.2). Geochemical data show the tephra is heterogeneous in composition but without distinct populations. The tephra has low silica content (average 60.3%) and high Al₂O₃, FeO and MgO with low K₂O. The tephra is similar in composition to the MP 27b population.

6.1.3 Interior & Western Alaska

Tephra layers were also located in the sites from western and interior Alaska. A single tephra layer was located in the Espenberg and Dot Lake B sites. In addition, three data sets were obtained from a large tephra layer in the Ahklun Mountains site. To assist correlation to the Aniakchak volcano, two proximal samples were also analyzed. EPMA data are shown in Table 6.1.3.

AKH 44. This sample is taken from the top of the major 11cm-thick tephra layer in the Akhlun Mountains site. EPMA data show this tephra is moderately silicic, and has more FeO, Al₂O₃ and TiO₂ than most of the tephras found in southeast Alaska. The sample is extremely similar in composition to AKH 65 and also very similar to AKH 46.
### Table 6.1.2: Electron Microprobe Data for Interior and Western Alaska Lepers Results as Zey pH Percentages from Beren (b)

<table>
<thead>
<tr>
<th>AKH</th>
<th>Data</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKH</td>
<td>44</td>
<td>46</td>
</tr>
<tr>
<td>AKH</td>
<td>65</td>
<td>38</td>
</tr>
</tbody>
</table>

Palaeoenvironmental Results
| DLB 11 | 12.0 | 13.05 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 | 21.0 | 22.0 | 23.0 | 24.0 | 25.0 | 26.0 | 27.0 | 28.0 | 29.0 | 30.0 |
|--------|------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| D       | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 | 21.0 | 22.0 | 23.0 |
| A       | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 |
| B       | 1.0  | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 |
| C       | 0.0  | 1.0  | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 |
| D       | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 | 21.0 | 22.0 | 23.0 |
| E       | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 |
| F       | 1.0  | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 |
| G       | 0.0  | 1.0  | 2.0  | 3.0  | 4.0  | 5.0  | 6.0  | 7.0  | 8.0  | 9.0  | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 15.0 | 16.0 | 17.0 | 18.0 |
AKH 65. This sample is taken from the base of the major tephra layer in the Akhlun Mountains site. The tephra is extremely similar in composition to AKH 44 and AKH 46 samples.

AKH 46. This sample is taken from the subsidiary tephra peak at 46cm in the Akhlun Mountains site. The tephra is extremely similar in composition to AKH 44 and AKH 65 samples.

ESP 38. This sample is taken from the visible tephra layer in the Espenberg site. EPMA data show the sample is very similar to all three of the Akhlun Mountains data sets.

DLB 11. This tephra is the only layer detected in the DLB site; it is a substantial sized micro-tephra (maximum concentration c.1x10^6 shards/gram dw.). EPMA data show the tephra to have two geochemical populations; a minor, more silicic population (those shards greater than 74% SiO₂ normalized, termed DLB 11a) and a more abundant less silicic population (shards under 72% SiO₂, termed DLB 11b). The minor silicic population is distinguished by less TiO₂, Al₂O₃, FeO, MgO and CaO and more K₂O.

In addition to the tephras from peatland sites, two proximal deposits of Aniakchak tephra were obtained from a coastal exposure on the northern Alaska Peninsula by USGS fieldworkers. These layers are believed to be from the c.3500BP caldera forming eruption and can provide information on the geochemistry of the proximal tephra, of use for correlation. The tephra bed consists of three layers, the lower two deposits were analysed:

NA-96b. This upper deposit is composed of lapilli approximately 5mm diameter, the layer is XXcm deep. The layer is similar in composition to many of the other analyzed western Alaska layers.

NA-96c. This lower deposit is a fine ash layer approximately XXcm deep. The layer is somewhat heterogeneous in composition, particularly with respect to Na₂O and SiO₂.
6.1.4 Data analysis

To identify correlations between tephra layers and determine their sources a variety of techniques were used including similarity coefficients, oxide plots and cluster analysis. The results are described region by region.

Southeast Alaska

The EPMA data for tephra layers have been compared quantitatively using similarity coefficients (Borchardt et al. 1972). Results are shown as matrices comparing tephras within the dataset and with the results of previous studies. Conventionally, coefficients greater than 0.95 are taken as indicative of the same tephra, coefficients between 0.90 and 0.95 may indicate different tephras from the same source (Begét et al. 1992). Considering the internal correlations, it can be seen that all the southeast Alaska tephra have some general similarity in composition, SCs are generally greater than 0.8 and many are greater than 0.9 (Table 6.1.4). The data need to be carefully interpreted with regard to the stratigraphic location of the layers. For instance, the highest SC value is 0.98 between the LNA 100 and LNA 39 layers. These tephra occur at different depths in the same site with no evidence for disturbance of the stratigraphy. It would therefore seem extremely unlikely that these layers are correlative. Similarly, quite high SC values are found between SPM 26 & MTR 146, SPM 26 & CHP 184, LNA 39 & MTR 146, ECR 32 & MTR 146 and ECR 32 & CHP 184. Given the difference in depth, and therefore probable age, these correlations seem unlikely. Correlations between ECR 100 & SPM26, ECR 100 & LNA 39, LNA 100 & SPM 26 and LNA 100 & ECR 32 also seem unlikely but cannot be so easily discounted on the basis of depth alone (Fig. 6.1.1).

Considering the SC results alone, some possible correlations are suggested. The data strongly suggest correlation between SPM 26, ECR 32 and LNA 39. SC values comparing these layers are generally high (>0.94) and the similarity in depth provides further support. The MTR 146 tephra may correlate with LNA 100 (SC=0.95), the CHP 184 layer may correlate with one or both of these layers (SC=0.95 and SC=0.92 respectively). It is possible, although unlikely that the ECR 100 tephra may correlate with
these layers (maximum SC=0.93 with MTR 146). The MTR 190 tephra has generally low SC values (<0.90) with the other tephras and probably does not correlate with any of the other layers. The ECR 162 tephra is clearly the most distinct with SC values <0.90, it is therefore unlikely to correlate with any of the other layers.

Table 6.1.4. Southeast Alaska, internal SCs

<table>
<thead>
<tr>
<th>Tephra</th>
<th>ECR 100</th>
<th>ECR 162</th>
<th>SPM 26</th>
<th>MTR 190</th>
<th>MTR 146</th>
<th>LNA 39</th>
<th>CHP 184</th>
<th>ECR 32</th>
<th>LNA 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECR 100</td>
<td>x</td>
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<td>0.90</td>
<td>0.82</td>
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<td>0.91</td>
<td>0.89</td>
<td>0.90</td>
<td>0.89</td>
</tr>
<tr>
<td>ECR 162</td>
<td>0.81</td>
<td>x</td>
<td>0.85</td>
<td>0.78</td>
<td>0.87</td>
<td>0.89</td>
<td>0.84</td>
<td>0.86</td>
<td>0.89</td>
</tr>
<tr>
<td>SPM 26</td>
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<td>0.85</td>
<td>x</td>
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<td>0.94</td>
<td>0.95</td>
<td>0.98</td>
<td>0.92</td>
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<tr>
<td>MTR 190</td>
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<td>0.95</td>
<td>0.96</td>
<td>0.95</td>
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<tr>
<td>MTR 146</td>
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<td>0.89</td>
<td>0.94</td>
<td>0.86</td>
<td>0.96</td>
<td>x</td>
<td>0.93</td>
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<td>0.90</td>
<td>0.95</td>
<td>0.93</td>
<td>0.97</td>
<td>x</td>
<td>0.92</td>
</tr>
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<td>0.95</td>
<td>0.90</td>
<td>0.95</td>
<td>0.93</td>
<td>x</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>ECR 32</td>
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<tr>
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<td>0.85</td>
<td>0.95</td>
<td>0.98</td>
<td>0.92</td>
<td>0.94</td>
<td>x</td>
</tr>
</tbody>
</table>

Data can also be investigated by oxide plots. Fig. 6.1.3 shows a FeO-TiO₂ plot of the normalized EPMA data from southeast Alaska. Several important features are evident. Most prominent of these is the clear separation of the ECR 162 analyses from the rest of the group; all of these data points lie in a region of higher FeO and TiO₂ in the upper right corner of the plot. The data from the other tephras are less well distinguished and occur within a broad group. There is however some suggestion that this broad group may be divisible in two, there appears to be a subgroup with FeO percentages <1.3 containing the majority of analyses from CHP 184 as well as some analyses from MTR 190, MTR 146, ECR 32, LNA 100 and LNA 39. The second sub-group with FeO percentages >1.3 contains fewer analyses from CHP 184 and more from LNA 39 and LNA 100. The MTR 146 analyses appear to be the most variable and are spread through a large part of the plot. The ECR 100 and MTR 190 analyses do not form truly distinct groups in this plot. Overall, this plot shows the clear differentiation of ECR 162 from the rest of the analyses but shows only limited evidence for differences between the other data sets. Fig. 6.1.4 shows a K₂O-FeO-CaO ternary plot using data set averages for all the analysed southeast Alaskan tephra layers. This plot shows a high degree of overlap between six of the data sets with the MTR 190, ECR 100 and ECR 162 tephras clearly distinguished.
Fig. 6.1.3 Fe/Ti plot for southeast Alaska tephras
Fig. 6.1.4 Ternary plot for southeast Alaska EPMA averages
Cluster analysis was used to further investigate the structure of the southeast Alaska EPMA data. Analyses were carried out for both the full data and averages for each tephra layer. For the full data, it is impractical to represent the results by dendrogram. Table 6.1.5 shows data grouping based on division at the 2nd level from the top (arbitrarily chosen). Four groups are recognized. Group one is much the largest group and includes the majority of the data: all analyses from the SPM 26, CHP 184 and ECR 32 data-sets and the majority of analyses from the LNA 39, LNA 100 and MTR 146 data-sets. One analysis of MTR 190 tephra is also included in this group. Group 2 includes all analyses of ECR 162 tephra and no others. Group 3 includes two analyses of LNA 100 tephra and one analysis of LNA 39 tephra. These analyses seem to be primarily differentiated from the rest of these data by low sodium content. Group 4 includes three analyses of MTR 146, both analyses of ECR 100 and one analysis of MTR 190 tephra. These analyses seem to be distinguished from other data by high SiO2 and/or low K2O.

**Table 6.1.5. Average-Link cluster analysis for full EPMA data, southeast Alaska**

<table>
<thead>
<tr>
<th>Group</th>
<th>Members</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>SPM 26 (6 analyses), LNA 39 (11 analyses), CHP 184 (12 analyses), LNA 100 (10 analyses), MTR 146 (15 analyses), ECR 32 (12 analyses), MTR 190 (1 analysis)</td>
</tr>
<tr>
<td>Group 2</td>
<td>ECR 162 (21 analyses)</td>
</tr>
<tr>
<td>Group 3</td>
<td>LNA 100 (2 analyses), LNA 39 (1 analysis)</td>
</tr>
<tr>
<td>Group 4</td>
<td>MTR 146 (3 analyses), ECR 100 (2 analyses), MTR 190 (1 analysis)</td>
</tr>
</tbody>
</table>

The cluster analysis illustrates some interesting features of the data. Overall, the groupings show reasonable agreement with those suggested previously. The SPM 26, LNA 39, CHP 184, LNA 100, MTR 146 and ECR 32 tephras are extremely similar to each other. Even at higher degrees of division, cluster analysis does not assign analyses to groups that are separable by stratigraphic or geographic location. The presence of some analyses of LNA 100, LNA 39 and MTR 146 in Groups 3 and 4 suggests these results are more variable. The Group 3 analyses are characterized by low sodium, these are likely to be analyses in which particular sodium mobilization occurred rather than a truly distinct group. The MTR 146 analyses in Group 4 could conceivably represent a minor population. The ECR 162 tephra is clearly distinguished from these tephras, all analyses are contained within a single separate group. The ECR 100 tephra is also reasonably well
Fig. 6.1.5 Cluster analysis dendrogram for southeast Alaska EPMA averages
distinguished, all analyses lying within Group 4. The analysis for the MTR 190 tephra assigns one sample to Group 1 and another to Group 4. This highlights the difference between these two analyses. The data-set is insufficiently large to determine whether this is due to heterogeneity of composition, poor analyses or even contamination.

The cluster analysis of the data-set averages shows a similar pattern, results are presented as a dendrogram in Fig. 6.1.5. At the first stage of the analysis, the MTR 146, CHP 184, SPM 26 and ECR 32 data-sets are combined together and the LNA 100 and LNA 39 sets combined with each other. At the second stage these two groups are combined together. In the third stage the MTR 190 and ECR 100 data-sets are combined. Subsequently the ECR 162 data-set is combined with the rest of the data. These results suggest close correlation between the MTR 146/CHP 184/SPM 26/ECR 32/LNA 39/LNA 100 data-sets. It is interesting to note that these results show the LNA 39 and LNA 100 tephras appear to be more closely related to each other than to the other tephras, which are only combined at the second stage. Results show some degree of correlation between MTR 190 and ECR 100 but this is limited, ECR 162 is clearly a distinct unit. Overall the results indicate that the ECR 100, MTR 190 and ECR 162 tephras are most likely to be separate from each other while there is a high degree of similarity between the other layers.

All tephra layers identified in this study were compared by similarity coefficients to a large data-set of tephra results compiled from previous Alaskan tephra studies (Riehle 1985, Riehle et al. 1987, 1990, 1992, 1999, Downes 1985, Begét et al. 1991b, 1992, Begét and Nye 1994, Richter et al.1995b, Beget & Motyka 1998, Child et al. 1998). Summary results are shown in Tables 6.1.6-6.1.11. The internal similarity coefficients, plots and cluster analysis suggest correlation between tephras SPM 26, ECR 32 and LNA 39. All of these tephras show a great deal of similarity to the White River Ash. SCs are as great as 0.99 with proximal WRA deposits and 0.96 with distal deposits (Table 6.1.6A). These SC values provide very good evidence for correlation. Correlations are not significantly better with either Northern or Eastern lobe data (Downes 1985).
The internal correlations also suggest possible correlation between two or more of CHP 184, MTR 146 and LNA 100. These tephras also show a good deal of similarity to White River Ash data. Similarity coefficients for all layers exceed 0.95 with at least one of the established data-sets (Table 6.1.6A). Evidence is most convincing with MTR 146 and LNA 100. With these layers SCs are greater than 0.95 with at least three WRA data-sets and are as high as 0.96 (LNA 100) and 0.97 (MTR 146). The SCs for the CHP 184 data-set exceed 0.95 with one proximal data-set and 0.93 with one proximal and one distal data-set. These values provide good evidence for these tephras to be the WRA or to have the same source. There is no great difference in correlation to the Northern or Eastern lobe data (Downes 1985). A ternary diagram comparing the averages of all these data sets (CHP 184, MTR 146, LNA 100, SPM 26, LNA 39 and ECR 32) with the White River Ash reference data shows a very good overlap (Fig. 6.1.4).

### Table 6.1.6B Southeast Alaska, SCs with other studies

<table>
<thead>
<tr>
<th></th>
<th>Augustine</th>
<th>Aniakchak</th>
<th>R. 89/90</th>
<th>R. 350 BP</th>
<th>R. 400</th>
<th>R. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECR  100</td>
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<td>0.94</td>
<td>0.92</td>
<td>0.78</td>
<td>0.77</td>
<td>0.79</td>
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<tr>
<td>ECR 162</td>
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<td>0.94</td>
<td>0.73</td>
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</tr>
<tr>
<td>MTR 190</td>
<td>0.78</td>
<td>0.77</td>
<td>0.77</td>
<td>0.93</td>
<td>0.93</td>
<td>0.95</td>
</tr>
</tbody>
</table>
The ECR 100, MTR 190 and ECR 162 tephras show only limited agreement with other layers and are likely to be distinct units. The microprobe data for ECR 100 is only from two shards, it is therefore somewhat difficult to make correlations. The highest SC values are with proximal Augustine tephra, values are ≤0.94 (Table 6.1.6B). SCs with distal Augustine tephra in Skilak Lake on the Kenai Peninsula (Beget et al. 1994) are lower (<0.90). As the SCs are all <0.95 firm correlation cannot be determined, however Augustine is probably the most likely source. The MTR 190 data-set is also only two analyses and the two shards are somewhat different from each other. The averaged composition shows a high degree of similarity to distal Redoubt tephra. SCs with the c.350BP, c.400BP and over 500BP Redoubt tephras at Skilak Lake (Beget et al. 1994) are over 0.96 with at least one data-set each. These SC values provide good support for a Redoubt origin of MTR 190 but the small number of analyses means that this must be treated with a degree of caution. The ECR 162 tephra is the most distinct analyzed tephra in the southeast Alaska sites. This tephra shows a reasonably high degree of agreement to distal Aniakchak tephra found in Western Alaska. SCs with four data-sets from previous studies in the northern Seward Peninsula are around 0.94 (Table 6.1.6B). This indicates a reasonable degree of correlation; similarity is very high for most oxides except Na₂O. This difference in sodium could conceivably be due to sodium loss in analysis rather than a true difference. SCs with four data-sets from southwest Alaska analysed in this study (AKH46, AKH44, AKH65, ESP 38) and assigned to Aniakchak are higher, between 0.95 and 0.98. These SCs with Aniakchak are considerably higher than with other major tephra layers investigated; it therefore seems extremely probable that Aniakchak is the source of this layer.

South-central Alaska

The similarity coefficients comparing among recovered south-central Alaskan tephras show generally limited agreement (Table 6.1.7). The majority of SCs are below 0.90 and some are as low as 0.51. The only SC value to exceed the 0.95 boundary is between MP 27b and MP 39, given the difference in depth and the stratigraphic integrity of this core the correlation seems unlikely. The second highest SC value is 0.92 between
MP 10a and ST 24. By the standards of Riehle (1985) this value could indicate correlation of volcanic source but not eruptive event. A TiO₂-FeO plot of all the south-central tephra data (Fig. 6.1.6) shows clear separation of the basaltic tephra MP 27b and MP 39 and indicates correlation between these two layers, but does not show clear differentiation within the more silicic tephras.

Table 6.1.7. South-central Alaska internal SCs

<table>
<thead>
<tr>
<th></th>
<th>ST 12</th>
<th>ST 24</th>
<th>ST 36</th>
<th>ST 68</th>
<th>MP 10a</th>
<th>MP 10b</th>
<th>MP 27a</th>
<th>MP 27b</th>
<th>MP 39</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST 12</td>
<td>x</td>
<td>0.84</td>
<td>0.87</td>
<td>0.88</td>
<td>0.71</td>
<td>0.69</td>
<td>0.57</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>ST 24</td>
<td>0.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>0.75</td>
<td>0.87</td>
<td>0.92</td>
<td>0.65</td>
<td>0.70</td>
<td>0.51</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>ST 36</td>
<td>0.75</td>
<td>0.75</td>
<td>x</td>
<td>0.83</td>
<td>0.81</td>
<td>0.76</td>
<td>0.73</td>
<td>0.6</td>
<td>0.61</td>
</tr>
<tr>
<td>ST 68</td>
<td>0.87</td>
<td>0.87</td>
<td>0.83</td>
<td>x</td>
<td>0.89</td>
<td>0.73</td>
<td>0.71</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>MP 10a</td>
<td>0.92</td>
<td>0.92</td>
<td>0.81</td>
<td>0.89</td>
<td>x</td>
<td>0.69</td>
<td>0.72</td>
<td>0.53</td>
<td>0.54</td>
</tr>
<tr>
<td>MP 10b</td>
<td>0.71</td>
<td>0.71</td>
<td>0.76</td>
<td>0.73</td>
<td>0.69</td>
<td>x</td>
<td>0.81</td>
<td>0.7</td>
<td>0.72</td>
</tr>
<tr>
<td>MP 27a</td>
<td>0.7</td>
<td>0.7</td>
<td>0.73</td>
<td>0.71</td>
<td>0.72</td>
<td>0.81</td>
<td>x</td>
<td>0.6</td>
<td>0.62</td>
</tr>
<tr>
<td>MP 27b</td>
<td>0.51</td>
<td>0.51</td>
<td>0.6</td>
<td>0.56</td>
<td>0.53</td>
<td>0.7</td>
<td>0.60</td>
<td>x</td>
<td>0.96</td>
</tr>
<tr>
<td>MP 39</td>
<td>0.5</td>
<td>0.5</td>
<td>0.61</td>
<td>0.57</td>
<td>0.54</td>
<td>0.72</td>
<td>0.62</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The Moose Pass tephras are rather distinct from other tephras in this study including tephras which are quite heterogeneous in composition and basaltic layers. Layer MP 10 contains two populations, the more silicic MP 10a and less silicic MP 10b. MP 10a shows a high degree of correlation with tephra from Mt. St. Augustine. SCs with Augustine 1883 tephra at Skilak Lake show values as high as 0.97, SCs with proximal Augustine tephra produce values up to 0.91 (Table 6.1.8). These results provide good evidence for an Augustine source. Population MP 10b shows limited similarity with other tephras, the highest SC values are with proximal Redoubt tephra but are under 0.90. Given the inter-mixing of the two populations, it is most likely that the MP 10b population is a secondary population within the Augustine tephra.

Layer MP 27 consists of a major mafic population (MP 27b) and a single more silicic shard (MP 27a). Of the Cook Inlet volcanoes, only Crater Peak on Mt. Spurr produces widespread mafic tephras (Child et al. 1998). Begét et al. (1994) identified two Crater Peak tephras at Skilak Lake, a layer dated to c.300BP and an older undated layer. MP 27b is extremely similar in composition to the c.300BP layer, SC values are as high as 0.98 (Table 6.1.8B). This provides extremely good evidence for a Crater Peak source. The MP 27a shard does not correlate well with other layers; the highest SC is only 0.84
Fig. 6.1.6 Fe/Ti plot for south-central Alaska tephras
with proximal tephra from Mt. Chiginigak, an improbable source. This shard may represent a minor geochemical population of Crater Peak tephra but could conceivably be from another source or even laboratory or field contamination.

Table 6.1.8A. South-central Alaska SCs with other studies

<table>
<thead>
<tr>
<th></th>
<th>Augustine 1883</th>
<th>Proximal Augustine</th>
<th>Proximal Redoubt</th>
<th>Chig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP 10a</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
<td>0.91</td>
</tr>
<tr>
<td>MP 10b</td>
<td>0.66</td>
<td>0.63</td>
<td>0.85</td>
<td>0.68</td>
</tr>
<tr>
<td>MP 27a</td>
<td>0.6</td>
<td>0.65</td>
<td>0.63</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Augustine 1883 = Augustine 1883 tephra at Skilak Lake (data-sets SK-10-2-7, SK-11-3-5 and SK-11-2-5: Begét et al. 1994)
Proximal Augustine = Proximal Augustine tephra on Augustine Island (data-sets CG-91-4-1A, RBW75A, RBW33D: Riehle et al. 1999)
Proximal Redoubt = Proximal Redoubt tephra, western Cook Inlet (data-sets 5-B, 5-C, 5-E: Riehle 1985)
Chig. = Proximal Mt. Chiginigak tephra (data-set 2RJ025E; Riehle et al. 1999)

Layer MP 39 consists of a single mafic population. The composition shows a high degree of similarity to MP 27b suggesting it is also of Crater Peak origin. SCs with the c.300BP layer at Skilak Lake are as high as 0.97, this strongly supports a Crater Peak origin although the SC values are slightly less than MP27b (Table 6.1.8B). The layer shows only a very limited similarity (SC=0.82) to the older Crater Peak tephra identified at Skilak Lake (Begét et al. 1994).

Table 6.1.8B. South-central Alaska SCs with other studies

<table>
<thead>
<tr>
<th></th>
<th>Crater Peak c.300BP</th>
<th>CP 500+</th>
<th>Crater Peak Proximal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP 27b</td>
<td>0.97</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td>MP 39</td>
<td>0.96</td>
<td>0.95</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Crater Peak c.300BP = c.300 BP Crater Peak-Mt Spurr tephra at Skilak Lake (data-sets SK-11-2-12, SK-11-3-13, SK-7-3-9, SK-7-4-8: Begét et al. 1994)
CP 500+ = >500BP Crater Peak-Mt Spurr tephra at Skilak Lake (data-set sk-6-1-53: Begét et al. 1994)
Crater Peak Proximal = Proximal Crater Peak-Mt Spurr tephra in western Cook Inlet (data-sets 20-E and 14-G: Riehle 1985)

Of the Sterling layers the ST 12 tephra shows the greatest similarity to Augustine tephras. The highest similarity is to the c.500 BP eruption (Augustine ‘B’), SCs are as high as 0.94 (Table 6.1.8C). Similarity to Augustine 1883 samples is more limited (SC<0.91). These values are less than the 0.95 criterion to define correlation of eruption but provide reasonable evidence for correlation of volcanic source.
### Table 6.1.8C. South-central Alaska SCs with other studies

<table>
<thead>
<tr>
<th></th>
<th>Katmai</th>
<th>Augustine 1883</th>
<th>Augustine B</th>
<th>Hayes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST12</td>
<td>0.84</td>
<td>0.86</td>
<td>0.83</td>
<td>0.91</td>
</tr>
<tr>
<td>ST24</td>
<td>0.94</td>
<td>0.94</td>
<td>0.95</td>
<td>0.91</td>
</tr>
<tr>
<td>ST36</td>
<td>0.72</td>
<td>0.60</td>
<td>0.71</td>
<td>0.80</td>
</tr>
<tr>
<td>ST68</td>
<td>0.82</td>
<td>0.73</td>
<td>0.81</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Katmai = Katmai 1912 tephra at Skilak Lake (data-sets SK-7-3-3p2, SK-7-3-3p1, SK-7-4-3p2: Begét et al. 1994)
Augustine 1883 = Augustine 1883 tephra at Skilak Lake (data-sets SK-10-2-7, SK-11-3-5 and SK-11-2-5: Begét et al. 1994)
Augustine B = Augustine c.500BP tephra at Skilak Lake (data-sets SK-7-4-11, SK-11-3-18, SK-10-2-32: Begét et al. 1994)
Hayes = Distal Hayes tephra at Tangle Lakes and Cantwell (data-sets TL8, ACT638 and ACT 638p2: Begét et al. 1991)

The source of the ST 24 tephra is uncertain. The highest SC values are with tephras attributed to Katmai 1912 (SC≤0.95; Table 6.1.8C). These values indicate a significant degree of similarity, however SC values are also relatively high with Augustine 1883 tephra (SC≤0.93). Katmai tephra has been noted to have a distinctive dual population; this is not noted in ST 24 (Begét et al. 1994). The tephra cannot be unambiguously assigned to a source but one of Augustine or Katmai would seem the most probable.

The ST 36 tephra shows the highest degree of similarity to the c.500 BP 'Augustine B' tephra SC values are as high as 0.92 (Table 6.1.8C). This does not show exact correlation but may indicate that the tephra is a different Augustine layer. The highest SCs with non-Augustine tephra are ≤0.85 with proximal Redoubt tephra (Riehle 1985). These results suggest that of the investigated tephras, an Augustine source is the most likely but this cannot be confirmed definitively.

The ST 68 tephra shows the best correlation with tephra attributed to Mt Hayes. The highest SC with Hayes tephra reaches the 0.95 criterion for correlation, SCs with two other data sets are only slightly lower (0.94). The highest SCs with non-Hayes tephra are with Augustine 1883 tephra (SC≤0.90). This therefore suggests a Hayes source for this tephra.

A CaO-K2O-FeO ternary diagram of south-central Alaska tephra averages and selected reference data (Fig.6.1.7) illustrates several of the previously mentioned findings. The MP 27b and MP 39 are closely correlated and agree well with Crater Peak data. The MP 10a tephra is very similar in composition to the Augustine 1883 tephra. The ST 12, ST 36 and MP 10b tephras are most similar to the Augustine B tephra but this is
Palaeoenvironmental Results

Fig. 6.1.7 Ternary plot for south-central Alaska EPMA averages

- Tephra layers in this study
- Selected other tephras
Palaeoenvironmental Results

not an exact correlation. The ST 68 tephra is most similar to the Hayes tephra. The ST 24 tephra bears a similarity to both the Augustine 1883 and Katmai 1912 tephras.

Interior & Western Alaska

The western Alaska tephras have also been compared with each other using similarity coefficients. The values are generally high, mostly exceeding 0.95. The AKH 46 and AKH 65 samples are most similar (SC=0.99; Table 6.1.9). These samples are from the top and base of the large Akhlun Mountains tephra layer, the high degree of similarity is therefore unsurprising. The subsidiary tephra peak (AKH 44) also shows a high degree of similarity to these samples (SC=0.97). This finding suggests that this layer is a secondary deposit from the same eruption rather than a distinct tephra. The tephra from the Espenburg site shows a high degree of similarity to the tephras at the Akhlun Mountains site (SCs≥0.97), strongly suggesting that they are from the same eruption. All the distal tephra data agree relatively well with the proximal NA-96 deposits from the Alaska peninsula (SCs≥0.94). The agreement is generally greater with the NA-96c tephra suggesting this as the more likely of the two deposits to represent the distal tephra-fall. A FeO-TiO₂ plot shows generally good overlap between the four distal data sets (AKH 44, AKH 46, AKH 65, ESP 38) strongly suggesting they are all the same tephra (Fig.6.1.8).

Table 6.1.9. Western Alaska internal SCs

<table>
<thead>
<tr>
<th></th>
<th>AKH 44</th>
<th>AKH 46</th>
<th>AKH 65</th>
<th>ESP 38</th>
<th>NA-96b</th>
<th>NA-96c</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKH 44</td>
<td>x</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>AKH 46</td>
<td>0.97</td>
<td>x</td>
<td>0.99</td>
<td>0.97</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>AKH 65</td>
<td>0.97</td>
<td>0.99</td>
<td>x</td>
<td>0.97</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>ESP 38</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>x</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>NA-96b</td>
<td>0.95</td>
<td>0.95</td>
<td>0.96</td>
<td>0.94</td>
<td>x</td>
<td>0.98</td>
</tr>
<tr>
<td>NA-96c</td>
<td>0.96</td>
<td>0.96</td>
<td>0.97</td>
<td>0.95</td>
<td>0.98</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 6.1.10 shows a SC matrix comparing these results with those of previous studies. Results provide good support for an Aniakchak origin of all these tephras. Comparison of all of these layers with the distal studies of Aniakchak tephra by Begét et al. (1992) and Riehle et al. (1987) produce high SC values, all but one of which exceed 0.95. In contrast SCs with other tephras found in interior Alaska do not exceed 0.90. A
Fig. 6.1.8 Fe/Ti plot for western Alaska tephras
K$_2$O-FeO-CaO ternary diagram also shows very good overlap between these tephras (Fig. 6.1.9). Given these correlations, the Akhlun Mountains and Espenberg tephras can be assigned to Aniakchak, and probably to the c.3500BP caldera-forming eruption.

<table>
<thead>
<tr>
<th>Table 6.1.10 Western Alaska, correlations with other studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniakchak</td>
</tr>
<tr>
<td>AKH 46</td>
</tr>
<tr>
<td>ESP 38</td>
</tr>
<tr>
<td>AKH 44</td>
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<tr>
<td>AKH 65</td>
</tr>
<tr>
<td>NA-96b</td>
</tr>
<tr>
<td>NA-96c</td>
</tr>
</tbody>
</table>

Aniakchak CE = Aniakchak at Cape Espenberg (Begét et al. 1992)
Aniakchak WL = Aniakchak at Whitefish Lake (Begét et al. 1992)
Aniakchak 7 = Aniakchak on southern Seward peninsula, site 7 (Riehle et al. 1987)
Aniakchak 8 = Aniakchak on southern Seward peninsula, site 8 (Riehle et al. 1987)
Jarvis = Jarvis Ash at Jarvis Creek (Begét et al. 1991)
WRA = White River Ash at Tok (Begét et al. 1992)
Oshetna = Oshetna tephra, Susitna River (Child et al. 1998)

The DLB 11 tephra in interior Alaska is difficult to assign to a source. The highest SC for population DLB 11a is with proximal White River Ash (SC=0.93, Table 6.1.11) however SCs are also relatively high with samples of Katmai, Redoubt and Augustine tephras (SCs≥0.93). Population DLB 11b shows the greatest similarity to proximal Redoubt tephra (SCs≥0.94). SCs do not exceed the 0.95 criterion with any of the comparison data-sets. Given the lack of good correlation and the number of tephras with moderate correlation, no source can be assigned.

<table>
<thead>
<tr>
<th>Table 6.1.11 Interior Alaska SCs with other studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katmai 1912</td>
</tr>
<tr>
<td>DLB 11a</td>
</tr>
<tr>
<td>DLB 11b</td>
</tr>
</tbody>
</table>

Katmai 1912 = Katmai 1912 tephra at Skilak Lake (data-sets SK-7-3-3-2 and SK-7-4-3-2: Begét et al. 1994)
R.'02 = Redoubt 1902 tephra (data-set 02nr: Begét et al. 1994)
Augustine '83 = Augustine 1883 tephra at Skilak Lake (data-sets SK-1-1-3-5 and SK-1-1-2-5: Begét et al. 1994).
WRA Ad = Distal White River Ash (Northern Lobe) in eastern Alaska (data-set 69-9: Downes 1985)
Proximal Redoubt = Proximal Redoubt tephra, western Cook Inlet (data-sets 5b, 5c and 5e: Riehle 1985)

Overall therefore these results suggest that tephras from many volcanoes have been located including Mt. Churchill, Mt. St. Augustine, Aniakchak, Mt. Spurr and
Fig. 6.1.9 Ternary plot for western Alaska EPMA averages
possibly other volcanoes including Mt. Hayes, Mt. Redoubt and Mt. Katmai. The most probable source of each tephra is summarized in Table 6.1.12. These results provide reasonable evidence for the sources of most of the tephras. However for some of the tephras, particularly the DLB 11 tephra and tephras in the Sterling site there is less certainty. Some of the difficulties in correlating tephras between studies may be due to differences in microprobe performance and techniques (Hunt & Hill 1996). In this study two different microprobes were used at Edinburgh and Bergen. Comparison of MP 39, MP 10 and LNA 39 tephras analyzed on each of the microprobes show reasonable agreement. When assessed by similarity coefficients values of 0.96, 0.96 and 0.97 are produced. Most elements are extremely similar with the exception of sodium for which values were markedly lower using the Bergen probe. This indicates that substantial sodium mobilization may have occurred using this machine. There are several possible reasons for differences in microprobe performance between studies as discussed by Hunt & Hill 1996. In this study the difference is almost certainly due to the use of a fixed beam in Bergen rather than a rastered beam as used for the majority of the analyses in Edinburgh.

Table 6.1.12 Summary- probable sources of microprobed tephras

<table>
<thead>
<tr>
<th>Tephra</th>
<th>Probable Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECR 100</td>
<td>Uncertain, possible Augustine</td>
</tr>
<tr>
<td>ECR 162</td>
<td>Aniakchak</td>
</tr>
<tr>
<td>SPM 26</td>
<td>WRA source</td>
</tr>
<tr>
<td>MTR 190</td>
<td>Possible Redoubt</td>
</tr>
<tr>
<td>MTR 146</td>
<td>WRA source</td>
</tr>
<tr>
<td>LNA 39</td>
<td>WRA source</td>
</tr>
<tr>
<td>CHP 184</td>
<td>WRA source</td>
</tr>
<tr>
<td>ECR 32</td>
<td>WRA source</td>
</tr>
<tr>
<td>LNA 100</td>
<td>WRA source</td>
</tr>
<tr>
<td>MP10</td>
<td>Augustine</td>
</tr>
<tr>
<td>MP27</td>
<td>Crater Peak- Mt Spurr</td>
</tr>
<tr>
<td>MP39</td>
<td>Crater Peak- Mt Spurr</td>
</tr>
<tr>
<td>ST12</td>
<td>Possible Augustine</td>
</tr>
<tr>
<td>ST24</td>
<td>Possibly Katmai or Augustine</td>
</tr>
<tr>
<td>ST36</td>
<td>Uncertain, possibly Augustine</td>
</tr>
<tr>
<td>ST68</td>
<td>Probable Hayes</td>
</tr>
<tr>
<td>DLB 11</td>
<td>Uncertain</td>
</tr>
<tr>
<td>AKH 44</td>
<td>Aniakchak</td>
</tr>
<tr>
<td>AKH 46</td>
<td>Aniakchak</td>
</tr>
<tr>
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<td>Aniakchak</td>
</tr>
<tr>
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<tr>
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<td>Aniakchak</td>
</tr>
<tr>
<td>NA-96c</td>
<td>Aniakchak</td>
</tr>
</tbody>
</table>
6.2 CHRONOLOGY
6.2.1 Radiocarbon results

Radiocarbon dates have been obtained from seven of these sites. These dates can be used to date the full-core and the tephra layers. Results are described site by site.

Mount Riley

One AMS date was obtained from towards the base of this site at 210cm (SUERC-564), the uncalibrated age is 8688 +/- 65 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 7940 and 7580 BC (9890 and 9530 BP). This indicates that peat initiation at the site started early in the Holocene.

Chilkoot Pond

Three AMS dates were obtained from this site. The lowermost date at 175cm (SUERC-565) has an uncalibrated age of 468 +/- 55 BP. OxCal calibration shows a 82.4% probability that the age of the sample is between 1380 and 1540 AD (570-410 BP). This date is extremely young in comparison to the other basal peat dates in southeast Alaskan sites. It is unlikely that this depth of peat could have accumulated in only 500 years and the peat appearance and to some extent the full core humification suggest that this date should be in the early Holocene. The date is therefore considered anomalous. Care was taken to avoid possible contamination in the laboratory and the field; although this cannot be ruled out it seems unlikely. An alternative possibility is that the samples might have been contaminated with 'young' carbon through rootlet penetration or bioturbation.

Two dates were obtained across the CHP 33 tephra layer. Date SUERC-5914 dated individually picked Sphagnum leaves and date SUERC-5919 dated Sphagnum stems. The two dates show good overlap. The date on leaves is 257 +/- 20BP, this calibrates to 1630-1670 AD (320-280 BP) with a 72.6% probability. The date on stems is 299 +/-24BP, this calibrates to 1490-1660AD (460-290 BP) with a probability of 95.4%.
These dates show a good overlap, the date on leaf material is more precise than that on stems.

**Spaulding Meadows**

One AMS date was obtained from this site at 196cm (SUERC-566), the uncalibrated age is 7207 +/- 53 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 6220 and 5990 BC (8170-7940 BP). This indicates that peat initiation started early in the Holocene but marginally later than the Eaglecrest, Point Lena and Mount Riley sites.

**Eaglecrest**

Three AMS dates were obtained from this site at 162cm on the ECR 162 tephra (SUERC-5917), at 195cm (SUERC-567) and at 365cm (SUERC-568). The uncalibrated age of the 162cm sample is 4485 +/- 30 BP. OxCal calibration shows a 92.1% probability that the age of the sample is between 3350 and 3080 BC (5300-5030BP). The uncalibrated age of the 195cm sample is 6183 +/- 56 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 5300 and 4990 BC (7250-6940 BP). The uncalibrated age of the lower sample is 9244+/- 49 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 8610 and 8310 BC (10,560-10260 BP). This date shows that peat initiation started in the very earliest Holocene.

**Point Lena**

One tephra layer in the Point Lena site was dated by radiocarbon. An AMS date at 100cm (SUERC-5913) had an uncalibrated age of 1428 +/-28BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 575 and 660 AD (1375-1290BP). Two further AMS dates were obtained from this site at 275cm (SUERC-569) and 520cm (SUERC-570). The uncalibrated age of the upper sample is 2423 +/- 51 BP. OxCal calibration shows a 76.2% probability that the age of the sample is between 670 and 390 BC (2620-2340 BP). The uncalibrated age of the lower sample is 7919+/- 83 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 7060
and 6630 BC (9010-8580 BP). This suggests that peat initiation started in the early Holocene.

Table 6.2.1 Radiocarbon dates

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<th>Code</th>
<th>Site</th>
<th>Technique</th>
<th>Sample</th>
<th>Depth (cm)</th>
<th>Age (BP)</th>
<th>Calibrated age range 1σ (BP)</th>
<th>Mid-point of calibrated age (BP)</th>
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<td>Mount Riley</td>
<td>AMS</td>
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<td>210-211</td>
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<td>9720</td>
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<td>Chilkoot Pond</td>
<td>AMS</td>
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<td>Spaulding Meadows</td>
<td>AMS</td>
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Sterling

One radiometric date was obtained from this site at 35-40cm (URCRM-1273). The uncalibrated date of the sample is 850 +/- 65 BP. OxCal calibration shows a 95.4% probability that the age of the sample is between 1030 and 1280 AD (920-670 BP).

Dot Lake B

Two samples were radiometrically dated at 20-25 and 40-45cm (URCRM-1272 and URCRM-1274). Both samples were reported as modern. The peat at this site is very lightly humified and is likely to represent recent peat accumulation. It is conceivable that the modern dates could show that the peat has accumulated post-1950 indicating an accumulation rate of almost 1cm per year. However this seems unlikely and it is more likely that the dates are aberrant. This could be due to contamination during sampling, transport or storage or through displacement of 'young' carbon in the field.

6.2.2 Age-Depth models

Outline age-depth models have been constructed for all the sites with dating evidence. Direct interpolation between the dating points is used due to the relative scarcity of dating evidence.

Mount Riley

An outline age-depth model for this site has been constructed using three time-markers: the surface taken to be the time of sampling (2002), the MTR 32 taken to be correlative to the CHP 33 tephra dated to c.300BP and the SUERC-564 radiocarbon date. Accumulation rates vary between 10 and 53 years/cm (Fig.6.2.1).

Chilkoot Pond

An outline age-depth model for this site has been constructed using two time-markers: the surface taken to be the time of sampling (2002), and the radiocarbon dated CHP 33 tephra. The radiocarbon date on the Sphagnum leaf material (SUERC-5914) has been used rather than the date on stem material due to the greater precision of this date.
Fig. 6.2.1 Age-depth plots for seven peatland sites. See text for full details of dating points, radiocarbon dates are shown as the mid-point of the calibrated age-range. Dashed lines show extrapolation below the lowest dating point.
Palaeoenvironmental Results

The lower date SUERC-565 was not used as it appears anomalous. Accumulation rate is shown to be around 10 years/cm. This would indicate peat accumulation starting less than 2000 years ago, this is surprisingly recent (Fig. 6.2.1). However with the extremely limited dating evidence it is not possible to be any more precise.

Spaulding Meadows

An outline age-depth model for this site has been constructed using three time-markers: the surface taken to be the time of sampling (2002), the SPM 26 tephra taken to be correlative to the CHP 33 tephra dated to c.300BP and the SUERC-566 radiocarbon date. Accumulation rates vary between about 13 and 45 years/cm (Fig. 6.2.1).

Eaglecrest

An outline age-depth model for this site has been constructed using five time-markers: the surface, the ECR 32 tephra taken to be c.300BP, the SUERC-5917 SUERC-567 and SUERC-568 radiocarbon dates. Accumulation rates vary between approximately 10 and 60 years/cm (Fig. 6.2.1).

Point Lena

An outline age-depth model for this site has been constructed using five time-markers: the surface, the LNA 39 tephra taken to be c.300BP, the SUERC-5913, SUERC-569 and SUERC-570 radiocarbon dates. Accumulation rates vary between approximately 9 and 25 years/cm, this is the highest rate of any of the sites with good dating evidence (Fig. 6.2.1).

Sterling

The available dating evidence for this site is just a single radiocarbon date. This indicates an accumulation rate of 21 years/cm with peat accumulation starting around 2000 BP (Fig. 6.2.1).
Moose Pass

An outline age-depth model has been constructed based on the only dating evidence - the MP 10 tephra layer taken to date to 1883. This indicates an accumulation rate of 12 years/cm (Fig. 6.2.1).
6.3 FULL CORE RESULTS

The full-core humification has been examined from four sites to place the results across the tephra layers in a wider context and investigate the Holocene palaeoclimate of the region. Humification results are described in terms of percentage transmission; this is the inverse of humification sensu stricto. Higher transmission values are taken as indicating wetter conditions.

Chilkoot Pond

The humification results from Chilkoot Pond show a distinct overall trend of increasing transmission values (Fig. 6.3.1). In the lowermost 50cm values fluctuate a great deal with peaks at 147.5 and 162.5cm and troughs at 142.5 and 157.5cm. Values are more stable between 127.5 and 137.5cm followed by a minor trough at 122.5 and then a more significant trough at 107.5. A peak is reached at 97.5cm before a period of more stable, lower values from 82.5 to 92.5cm (around 36% transmission). This is followed by a marked rise and then stable values between 77.5cm and 47.5cm (around 39% transmission). This period is followed by an increase to reach a minor peak at 42.5cm and then a more significant peak at 32.5cm. This peak marks the highest values of the profile (42.6%) and is followed by a decline to a trough at 27.5cm; more stable, higher values are present from 22.5 to 7.5cm (around 41%) with lower values in the uppermost sample.

Fig. 6.3.2 shows the data de-trended and interpreted using the age-depth model. The limited nature of the age-depth model means that the age estimates must be treated with considerable caution. The results show rapidly fluctuating values from the base of the profile to c.850BP with more stable higher values from c.1350-1500BP and more stable lower values from c.850-1000BP. At around 850BP there is a pronounced wet shift with more stable higher values to c.500BP. From c.500BP values increase reaching a peak at c.350BP. From this point values decline and fluctuate to c.80BP, the most recent sample has a lower value.
Fig. 6.3.1 Full core humification results from four sites in southeast Alaska expressed as percentage transmission.
Spaulding Meadows

The humification record from the Spaulding Meadows site (Fig. 6.3.1) is dominated by a very obvious change in the middle of the sequence. From the base of the profile to 127.5cm there is little overall trend in values with minor troughs at 162.5 and 182.5cm and higher values between 142.5 and 157.5cm. Between 122.5 and 112.5cm values are lower and relatively stable (around 23% transmission). From 112.5 to 87.5cm there is a large and sustained increase in values of over 13%. This increase is followed by more stable values to 37.5cm with values fluctuating around 36% transmission. From a minor peak at 42.5cm, values decline consistently to a trough at 27.5cm. This is followed by a minor peak at 22.5cm and then a further decline to a trough at 17.5cm (<30% transmission). Values increase through the final three data points returning to around 36% by the uppermost sample.

The de-trended and dated profile is shown in Fig. 6.3.2. The results show declining values from the base of the profile to c.4700BP followed by more stable values to c.4200BP. At this point there is a very pronounced wet shift lasting to c.3000BP, values continue high to c.2500BP. From c.2000 to c.1000BP values are lower than previously. From 1000 to c.250BP values fall very rapidly with a minor peak at c.300BP. In the upper samples values recover back towards previous values.

Eaglecrest

The humification record from Eaglecrest peatland shows several distinct phases (Fig. 6.3.1). From the base of the profile to 247.5cm values gradually decline from over 30 to under 25% transmission. Values are slightly higher and relatively stable from 242.5 to 127.5cm around 28% transmission. From 112.5 to 122.5cm there is a brief period of lower but more stable values (<26%). From 112.5 to 97.5cm values increase by over 6%. From 97.5 to 82.5cm values are high and relatively stable around 31% transmission. Between 82.5 and 77.5cm there is a rapid drop in transmission values to 26%, values
Fig. 6.3.2 Detrended full core humification results interpreted using age-depth models. Results expressed as residuals from a linear regression. Dashed lines show probable correlations between sites, dotted lines show possible correlations. Results for Chilkoot Pond site are unreliable due to limited dating evidence.
continue low to 57.5cm. Through the top 50cm of core there is a continued increase in values reaching over 39% transmission in the uppermost sample.

The de-trended and dated results are shown in Fig. 6.3.2. The results show a declining trend at the base of the profile to c. 8000BP, values fluctuate to around 7000BP. There is a period of greater stability between around 4200 and 6600BP followed by a drop in values and a period of lower stable values between c. 3700 and 3300BP. Between c. 3300 and 2700BP there is a marked wet shift with higher values continuing to c. 2100BP. Values drop markedly (a dry shift) between c. 2100 and 2000BP with a subsequent minor increase to a small peak at c. 1400BP. Values drop again at c. 1200BP and then increase to the top of the profile.

Mount Riley

The humification results for the Mount Riley peatland are shown in Fig. 6.3.1. From the base of the profile to 177.5cm there is a slight decline in values, this is followed by a rapid increase to 172.5cm and then a slower increase reaching a peak at 152.5cm of 35.5% transmission. Values drop markedly to the 142.5cm sample before recovering in the 137.5cm sample. Values fall again to the 127.5cm sample to under 24%. Values remain low from 127.5 to 112.5cm at around 24%. Values increase again to reach a peak at 97.5cm (30.7%) and then remain high to 67.5cm. From 67.5 to 62.5cm values fall by over 5% transmission, values remain low to 57.5cm and then increase to reach a peak at 42.5cm (28.6%). Values fall to 32.5cm and remain low in the 27.5cm sample (around 24%). In the five uppermost samples there is a pronounced increase, reaching the highest value of the profile in the upper sample (>40% transmission).

The de-trended and dated results are shown in Fig. 6.3.2. Values are relatively low at the base of the profile with a distinct wet shift around 7900BP, a more gradual increase in values continues to c. 6600BP. Values undergo a general decline to c. 5300BP and then a stable drier period to c. 4500BP. Between c. 4500 and c. 3700BP there is a pronounced wet shift with higher values continuing to c. 2100BP. At 2100BP there is a distinct dry shift followed by an increase to a peak at c. 800BP. Values drop again around 300BP and
then increase to the top of the profile. These results are discussed in the subsequent chapter.
6.4 RESULTS ACROSS TEPHRA LAYERS

The palaeoecological record across the tephras recovered from sites in southeast and south-central Alaska has been investigated. Testate amoebae analysis was not possible at all sites due to a very low test concentration. The tephra layers found in interior and western Alaska have not been studied as the peat conditions are not optimal for palaeoecological study. Full details of analyses carried out are summarized in Table 6.4.1.

6.4.1 Tephra layers with full palaeoecological data

Complete set of palaeoecological data including testate amoebae, humification and macrofossil data was obtained for eleven tephra layers.

CHP 33

The humification results across the CHP 33 tephra are shown in Fig. 6.4.1. Results show rapidly fluctuating transmission values at the base of the core. Three transmission peaks are reached in the lower half of the core at 34.75, 35.75 and 37.25cm. From 34.75cm there is a rapid decline in transmission values, to 32% at 32.75cm although a brief peak at 33.75cm interrupts this trend. From this point there is a prolonged increase to reach a peak at 30.75cm; the final sampling point at 28.25cm shows still greater transmission (38.2%). The tephra layer in this profile reaches a peak concentration around 33-34cm. This point occurs directly after a significant decline in transmission values and around 1cm below the start of a trend of increasing transmission values.

The CHP 33 testate amoebae diagram (Fig. 6.4.2) shows a testate amoebae assemblage dominated by *Hyalosphenia papilio* (values from 28 to 61%). From 41 to 37cm depth the testate amoebae community is characterized by moderately high amounts of *H. papilio* with significant amounts of *Amphitrema flavum* (around 6%), *Nebela tincta* (around 12%) and *Nebela militaris* (around 8%). Appreciable but variable quantities of
Fig. 6.4.1 Summary of the palaeoecological data across the CHP 33 tephra. Showing, tephra concentration as shards per gram dry weight, humification expressed as corrected percent transmission (raw values shown dotted), testate amoebae inferred depth to water table (TI-DWT), testate amoebae inferred pH (TI-pH) and macrofossil peat components. See text for full detail of methodologies.

Fig. 6.4.3 Summary diagram for the ECR 100 tephra. Details as for CHP 33.

Fig. 6.4.5 Summary diagram for the ECR 162 tephra. Details as for CHP 33.

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Table 6.4.1. Summary of palaeoecological research carried out, by tephra layer.

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<thead>
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<th>Tephra</th>
<th>EPMA</th>
<th>Humification</th>
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<th>Macrofossils</th>
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+ This section of the core was damaged in transit, accurate determination of the tephra depth and palaeoecological work was not possible.
* This tephra occurred at the junction of two cores, palaeoecological research was not possible.
$ This tephra occurred at the very base of the profile, palaeoecological analyses were not possible.
- Analysis was carried out but is not presented here.

Arcella catinus and Trigonopyxis arcula and smaller numbers of Assulina muscorum, Bullinularia indica and Centropyxis aculeata are also present. The sample at 35.5cm is notable for a significant increase in the abundance of H. papilio, following this peak there is a gradual return to previous values by the 30.5cm sample. From 36cm there is the start of a period of gradual increase in Aflavum reaching a peak at 30.5cm of over 27%. Above 36cm there are several samples with no N.tineta and when this species returns it is less abundant than previously. B.indica reaches a peak of over 15% in the 36.5cm sample...
Fig. 6.4.2 Testate amoebae diagram across the CHP 33 tephra layer. Species shown as percentage of total count, horizontal line marks tephra peak.

A) CHP 33

Fig. 6.4.4 Testate amoebae diagram for the ECR 100 tephra. Details as for CHP 33.

B) ECR 100

Fig. 6.4.6 Testate amoebae diagram for the ECR 162 tephra. Details as for CHP 33.

C) ECR 162
and is also high in the subsequent sample, however for the rest of the sequence values are broadly constant. Above 35.5 cm there is an increasing proportion of *Phryganella acropodia*, reaching a peak at 30.5 cm of over 17%, there a moderate decline following this peak. In the uppermost five centimeters of the sequence there is a loss of *C. aculeata* and a marginal reduction in frequency of *Trigonopyxis arcula*. Above 30.5 cm there is a gradual decline in *A. flavum* with the species reaching its lowest abundance in the sequence in the upper sample at 26.5 cm. Coincident with this decline in *A. flavum* is a resumed increase in *H. papilio* above 30 cm reaching its highest values in the profile in the uppermost sample (61%). In the uppermost two centimeters of the sequence there is notably more *Assulina muscorum* than in previous stages. Of the minor species, it is notable that all the *Difflugia* species *Heleopera petricola* and *Nebela tubulosa* only occur in the lower half of the sequence while *Assulina seminulum* and *Centropyxis ecornis* only occur in the upper half of the sequence.

The tephra peak in this core occurs at 33.5 cm. There are some changes in the testate amoebae community at around this period but they are relatively subtle. Above 33.5 cm there is the start of an increase in *A. flavum* reaching a peak at 30.5 cm, coincident with this there is an increase in abundance of *P. acropodia*. There are also changes in abundance of some minor species with fewer occurrences above the tephra, such as the *Difflugia* species. The overall changes could be interpreted as a slight shift towards wetter conditions following tephra deposition although the changes are relatively subtle.

Testate amoebae results have been interpreted quantitatively using transfer functions. For the DWT transfer function between 93 and 100% of testate amoebae are included (average 97.5%), for the pH transfer function between 90 and 100% are included (average 97.5%). The TI-DWT results (Fig. 6.4.1) show a general trend of increasing values from the base of the profile to 36.5 cm with rather lower values at 37.5 cm. Between 35.5 and 36.5 cm there is a marked drop in values, a reduction of 9 cm TI-DWT. From 31.5 to 35.5 cm values are more stable at around 40 cm. Between 31.5 and 30.5 cm there is a further reduction of 7 cm, above this values increase initially slowly and then more rapidly reaching over 40 cm TI-DWT at 27.5 cm, the uppermost sample has a marginally lower TI-DWT. The tephra peak occurs in a region of relatively stable TI-DWT values. The TI-pH results (Fig. 6.4.1) show a rapid decline at the base of the profile.
between 40.5 and 39.5 cm. From 39.5 to 35.5 cm there is a gradual increase, returning to over 4.2 at 35.5 cm. Between 35.5 and 30.5 cm values are lower with a trough centred at 32.5 cm. From 29.5 cm, values decline towards the top of the core. The tephra peak at 33.5 cm occurs in a region of declining pH values i.e. a zone of increasing acidity.

The macrofossil results (Fig. 6.4.1) show that the peat at this site is heavily Sphagnum dominated throughout this section (>85%). From the base of the profile to 35 cm, the peat also contains a few percent monocotyledon remains (1-7%) and UOM (2-6%). The sample at 35.5 cm contains notably more UOM than below (10%). From this point to 32.5 cm there is a reduction in the extent of monocots and UOM. In the upper half of the profile there is less than 2% of either monocots or UOM. The tephra peak at 33.5 cm is broadly synchronous with this apparent reduction in extent of monocots and UOM. This change is relatively small and may be less than the errors inherent in the method.

**ECR 100**

The humification data across the ECR 100 tephra are shown in Fig. 6.4.3. From the base of the section values increase reaching a peak of 23% at 103.25 cm. Above this peak there is a gradual decline to 100.75 cm (20%), this depth marks the shift to a trend of increasing values. Values increase to an initial peak of 23.98% at 99.25 cm. After this initial peak, values steady out again before another rapid increase, to reach a second and higher peak at 96.75 cm, 27.44%. Above this peak, there is an even more rapid and pronounced decrease to the top of the section. The tephra layer in this core reaches a peak concentration at 100-101 cm. This depth marks a change from declining transmission values to increasing transmission values. The initial increase above the tephra is of a similar magnitude to the decline below the tephra, however this is followed after 1.5 cm by a more significant increase to a much higher peak.

The testate amoebae data across the ECR 100 tephra are shown in Fig. 6.4.4. The most abundant testate amoebae species at this site is Amphitrema flavum, which exceeds 20% of the total for much of the examined section. From the base of the profile to 101 cm, the community structure is relatively stable with around 30% Amphitrema flavum, 12 to
15% *Hyalosphenia papilio* and *Phryganella acropodia* and smaller but consistent occurrences of *Habrotrochoa angusticollis*, *Centropyxis aculeata*, *Assulina muscorum*, *Amphitrema stenostoma* and *Amphitrema wrightianum*. From 101 cm there are changes in several species. From 101 to 98 cm there is a reduction in *Aflavum* abundance, followed by an increase to give the highest levels in the profile in the uppermost centimetre. From 101 to 96 cm there is substantially more *P. acropodia*, around twice the abundance of lower in the core. Also from 101 cm there is the first appearance of *Difflugia tuberculata* in the profile. Several other species have notably reduced abundance and frequency of occurrence above 101 cm including *C. aculeata*, *H. papilio* and *H. angusticollis*. The uppermost sample is notable for elevated abundances of *H. papilio* and *A. flavum*. The tephra layer in this profile reaches a peak at 100.5 cm. This is coincident with many of the major testate amoebae changes, most notably the declines in *H. papilio* and *A. flavum* and increases in *P. acropodia* and *D. tuberculata*. A qualitative interpretation would suggest this as a shift to drier conditions primarily due to the declines in *A. flavum* and *H. papilio*, both of which are good indicators of wetter conditions.

Testate amoebae results have been quantitatively interpreted using transfer functions. For both the DWT and pH transfer functions between 90 and 100% of testate amoebae are included (average 95.4%). The TI-DWT results across the ECR 100 tephra are shown in Fig. 6.4.3. Data show a small drop from the lowermost sample to the 103.5 cm sample, this is followed by a sharp rise to the 102.5 cm sample, values increasing by over 6 cm TI-DWT. From 102.5 to 100.5 cm values are more stable; around 27 cm TI-DWT. Between 100.5 and 99.5 cm there is a sharp increase in TI-DWT values from 26.5 to 33.7 cm. From this point to the top of the profile, values gradually decline with a minor peak at 96.5 cm. At the top of the section the TI-DWT value is 27 cm. The tephra peak at 100.5 cm coincides with a sharp increase in TI-DWT values representing a move to drier peat surface conditions. The TI-pH results show a trend which is almost opposite that observed for TI-DWT (Fig. 6.4.3). From the base of the profile an initial increase is followed by a more substantial decrease and then more stable values between 100.5 and 102.5 cm. The largest change of the profile is a decrease of almost 0.3 between 100.5 and 99.5 cm. From 99.5 to 97.5 cm there is a gradual increase in values returning to 4.7, there
is a greater degree of stability in the upper three samples from 97.5 to 95.5 cm. The tephra peak occurs just below a sharp shift to lower values representing more acidic conditions.

The macrofossil results across this tephra are shown in Fig. 6.4.3. The diagram shows monocotyledon domination through the lower two thirds of the core followed by a switch to Sphagnum domination. From the base of the profile to 97.5 cm the peat is composed of around 5-20% Sphagnum, around 60-80% monocots, around 10% UOM and 5% Ericales. From 97.5 cm there is a rapid increase in Sphagnum abundance reaching 75% in the uppermost sample. Coincident with this increase there is a loss of monocotyledons, down to under 20% and more subtle declines in UOM and Ericales. Above the tephra peak there is a minor increase in Sphagnum but this is small compared to the later change.

**ECR 162**

The humification data across the ECR 162 tephra is shown in Fig. 6.4.5. From the base of the profile there is a brief increase in values to a peak at 166.75 cm (25%). Above this peak there is a gradual decrease in values to 162.75 cm (19%) although this decline is not uniform. From 162.75 cm the overall trend switches to one of increasing values. This increase is initially sharp but slows to reach a peak at 160.25 cm. At the top of the profile, values decline from the peak at 160.25 cm before increasing to a second peak at 158.25 cm and then declining again. The tephra layer in this profile reaches a peak concentration at 162-163 cm. This depth broadly coincides with the change from a gradual decrease in values through much of the lower half of the profile to an increase in the upper half of the profile.

The testate amoebae data across the ECR 162 tephra is shown in Fig. 6.4.6. From the base of the sequence to 166 cm the community is characterized by abundant (>50%) *Amphitrema flavum*. Also present are moderate amounts of *Hyalosphenia papilio* and *Habrotrocha angusticollis* and more minor quantities of *Centropyxis aculeata*, *Cyclopyxis arcelloides*, *Assulina muscorum*, *Amphitrema wrightianum* and *Amphitrema stenostoma*. From 166 to 163 cm it is notable that *Centropyxis aculeata* and *Cyclopyxis arcelloides* are largely lost while other major species remain broadly as below. From 163 cm there are several highly noticeable changes. Perhaps most distinct of these is a
marked decline in *A. flavum* from around 50% to around 25%. Also at this time are marked increases in *Bullinularia indica*, *Heleopera sphagni* and *H. angusticollis*. *A. flavum* reaches a minimum at 159.5 cm, *B. indica* and *H. angusticollis* also peak around this point. From 159.5 cm to the uppermost sample at 155.5 cm there are declines in *H. angusticollis* and *B. indica* and in the final sample a return of more abundant *A. flavum* (47%). This uppermost part of the profile is also marked by a brief phase of *P. acropodia* with the species first found in significant numbers at 159.5 cm, reaching a peak of over 23% at 157.5 cm and declining again towards the top of the sequence. The tephra concentration profile reaches a peak at 162.5 cm. This point is very close to many of the major changes in this sequence, although some changes seem to start in the sample below the peak, the *A. flavum* decline most notably. The shift above the tephra from *A. flavum* towards *H. sphagni*, *H. angusticollis*, *B. indica* and *P. acropodia* would be qualitatively interpreted as a change to drier conditions.

Testate amoebae results have been quantitatively interpreted using the new Alaskan transfer function. For both the DWT and pH transfer functions between 89 and 100% of testate amoebae are included (average 98.8%). TI-DWT results (Fig. 6.4.5) show generally stable values between the base of the profile and 163.5 cm. The sample at 162.5 cm shows a minor peak (28 cm) with lower values at 161.5 cm (23 cm). From 161.5 to 160.5 cm there is a substantial increase in TI-DWT values of 11 cm. TI-DWT at 159.5 cm is also high, this is followed by a much lower value at 158.5 cm (under 21 cm). At 157.5 cm values increase to over 30 cm with values gradually declining to the top of the profile. The tephra peak at 162.5 cm coincides with a TI-DWT peak representing a shift to assumed drier conditions. This peak is relatively small compared to the more major TI-DWT change between 160.5 and 161.5 cm. TI-pH results are shown in Fig. 6.4.5. The trends in TI-pH are largely the inverse of the pattern for TI-DWT. From the base of the profile to 163.5 cm there is little overall trend with values around 4.8. Between 163.5 and 162.5 cm there is a drop in values of around 0.2. Values remain lower to 159.5 cm with a minor peak at 161.5 cm. Between 159.5 and 158.5 there is a substantial increase in TI-pH with values reaching over 5. The sample at 157.5 cm has a much lower inferred pH (4.6) with values returning to around 5 for the uppermost two samples. The sample containing
the tephra peak has low inferred pH (relatively acidic conditions) and occurs immediately after a drop in TI-pH values.

The macrofossil results across this tephra are shown in Fig. 6.4.5. These results show that the majority of the peat is made up of monocots. From the base of the profile to 162.5 cm there is a gradual decline in *Sphagnum* and the greatest abundance of Ericales. From 162.5 cm to the top of the profile there is more *Sphagnum* (around 15%), this increase is largely at the expense of UOM which is reduced to around 20%. The tephra peak at 162.5 cm is notable for a total absence of *Sphagnum* preceding an increase to greater abundance in the upper half of the core. This sample is also distinct for having much the greatest abundance of UOM in the profile (41%).

**LNA 39**

The humification results across the LNA 39 tephra show one of the greatest changes of any profile (Fig. 6.4.7). From the base of the profile to 39.75 cm there is a high degree of consistency in results with transmission values between 20 and 24% transmission. From 39.75 to 39.25 cm there is a decrease in values to 17%; values remain lower to 38.25 cm. From 38.25 cm there is a significant and sustained increase in values to reach a major peak at 36.75 cm (33.5%). Values remain consistently high to the top of the examined section at 35.25 cm. The large change in this profile represents a transmission increase of over 17%, a highly significant change. The tephra profile for this site is complex; a maximum value is reached at 39-40 cm. This point coincides with a minor decline in transmission and occurs around 1 cm below the start of the major increase in values.

The testate amoebae data across the LNA 39 tephra are dominated by three *Amphitrema* species; *A. flavum, A. wrightianum* and *A. stenostoma* (Fig. 6.4.8). At the base of the profile from 44 cm down, the community is heavily dominated by *A. flavum* (over 40%). At this stage *A. wrightianum* and *A. stenostoma* are virtually absent while *A. muscorum, A. seminulum, T. arcula* and *H. angusticollis* are at their most abundant levels. At around 44 cm there is a distinct change with a drop in *A. flavum* abundance of over 30%. Coincident with this are rapid increases in *A. stenostoma* and *A. wrightianum* and a rather reduced abundance of *A. muscorum* and *A. seminulum*. From 44 to 37 cm the
Fig. 6.4.7 Summary diagram for the LNA 39 tephra. Details as for CHP 33.

Fig. 6.4.9 Summary diagram for the LNA 100 tephra. Details as for CHP 33.

Fig. 6.4.11 Summary diagram for the ST 12 tephra. Details as for CHP 33 with the exception of tephra concentration, results are shown here as loss on ignition, the trough represents the tephra layer.

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most abundant testate amoebae species is *A. stenostoma*, reaching levels of over 40%; *A. wrightianium* is also abundant in this stage with values fluctuating around 20%. This region of the profile is also noticeable for the presence of *C. aculeata, N. tinctoria* and *P. acropodia*. From around 37-35cm there is a second distinct change in the testate amoebae community. *A. flavum* returns to its former abundance (over 50%), largely replacing *A. stenostoma* and *A. wrightianum* which both decline significantly. This depth also marks the start of a rapid increase in *H. papilio*, expanding to over 29% by the uppermost sample, making it the second most abundant species. Comparison with the tephra concentration is difficult due to the complexity of the tephra profile at this site. The highest tephra concentration is at 39.5cm but tephra is abundant for around 10cm. At the tephra peak at 39.5cm there are no particularly distinct changes in testate amoebae community. The major changes are below the tephra peak (around 44cm) and above the tephra peak (around 36cm). While it is possible that these changes are related to tephra deposition, the tephra profile and probably complex pattern of tephra taphonomy mean that this cannot be reliably determined.

Testate amoebae results have been quantitatively interpreted using transfer functions. For the DWT transfer function between 94 and 100% of testate amoebae are included (average 98.7%), for the pH transfer function between 97 and 100% are included (average 99%). Results are shown in Fig. 6.4.7. The data shows a sharp increase of 8cm TI-DWT between the base of the profile and the next sample at 45.5cm. Between 45.5 and 43.5cm there is a major decline in TI-DWT values of over 10cm. From 43.5 to 41.5cm values are relatively stable around 27cm TI-DWT. The sample at 40.5cm has a lower value of under 23cm but values increase again to the samples at 39.5 and 38.5cm (around 29cm TI-DWT). From 38.5 to 37.5cm there is a substantial decline of around 7cm TI-DWT, values remain low (around 22-24cm) to the top of the profile at 32.5cm. These results show a very substantial overall wet shift in this profile, a change of up to 16cm TI-DWT in total. The tephra peak at 39.5cm occurs after the major wet-shift, this sample coincides with a shift to assumed drier conditions (TI-DWT increase of around 6cm). The TI-pH results show an initial small decline in values with a pronounced increase between 45.5 and 40.5cm. From this peak, values decline to 38.5cm (a decrease of almost 0.2) and then recover to a peak at 37.5cm. From this point to the top of the
Fig. 6.4.8 Testate amoebae diagram for the LNA 39 tephra. Details as for CHP 33.

D) LNA 39

Fig. 6.4.10 Testate amoebae diagram for the LNA 100 tephra. Details as for CHP 33.

E) LNA 100

Fig. 6.4.12 Testate amoebae diagram for the ST 12 tephra. Details as for CHP 33.

F) ST 12
profile there is a trend of gradually declining values. The tephra peak at 39.5cm occurs within a region of declining TI-pH values representing a shift to assumed more acidic conditions.

The macrofossil results show a great deal of variability in peat composition (Fig.6.4.7). From the base of the profile to the 41.5cm sample there is a trend of declining Sphagnum content, reduced from 70% to 26%. Through this stage, there is an increase in monocot abundance from 19 to 65%. UOM content increases from low values in the lower samples to 23% at 42.5cm, Ericales values are as high as 11% in this stage. From 41.5cm there is a change to a trend of gradually increasing Sphagnum content and decreasing monocot content; a brief peak of Sphagnum at 39.5cm interrupts this trend. A peak of UOM content is reached at 38.5cm of 28%; following this UOM values generally decline. From 35.5cm the peat is heavily Sphagnum dominated (over 90%) with small amounts of monocots (<8%) and Ericales (<3%), UOM is virtually absent. This heavily Sphagnum-dominated assemblage continues to the top of the profile. The tephra peak at 39.5cm occurs after the start of the Sphagnum increase, this point coincides with a minor Sphagnum peak and occurs immediately below a UOM peak.

LNA 100

The humification profile across the LNA100 tephra shows significant change (Fig.6.4.9). From the base of the profile at 107.25cm until 101.25cm, there is a gradual decline in transmission values from 29.6 to 21.9%. This general decline is punctuated by three minor peaks at 103.25, 105.25 and 106.25cm. From 101.25 to 99.75cm there is a major increase of 10.2% transmission. The peak at 99.75cm shows the highest transmission values through the entirety of the profile. Above this peak, there is a significant decline for the next two data points down to 25.24% transmission. From 98.75 to 96.25cm there is a gradual increase in transmission to a peak of 30.7% at 96.25cm. Transmission in the uppermost sample is somewhat reduced. The tephra layer in this profile shows a peak concentration at 100-101cm. This coincides with the central phase of the major increase in transmission values from 101.25 to 99.75cm.

The testate amoebae data across the LNA 100 tephra layer are shown in Fig.6.4.10. The testate amoebae community in this core is dominated by A.flavum, from
103-106 cm values exceed 50%. Abundant species in this lower section of the core also include *A. muscorum, A. seminulum, B. indica, C. oviformis* and *Difflugia pulex*. From 103 cm to 101 cm there is a marked decrease in abundance of *A. flavum* by around 20%, coincident with this is an increase in *Difflugia pulex*, reaching a peak of over 20% at 102.5 cm. From 101 cm there is a further change with an increase in *A. flavum* abundance to over 45%. Above 101 cm there is increasing occurrence of *A. stenostoma* and *A. wrightianum*, species which are rare lower in the profile. There is also increased abundance of *A. muscorum, H. papilio* and *H. angusticollis* in this upper section of the core. The most distinct change in testate amoebe assemblage within this profile is the loss of *D. pulex* at 101 cm. This species declines from over 18% of the total in the 101.5 cm sample to none in the 100.5 cm sample, the species is only found in one sample above 101 cm. The tephra profile for this core shows a distinct tephra peak at 100.5 cm. This point is coincident with several changes including the increase in *A. flavum*, the establishment of *A. stenostoma* and *A. wrightianum* and the loss of *D. pulex*. A qualitative interpretation of the data would suggest a shift to drier conditions from 103 to 101 cm with the reduction in *A. flavum* and expansion of *D. pulex*. This is followed by a shift back to wetter conditions from 101 to 99 cm with the increase in *Amphitrema* species. The greater abundance of *A. stenostoma* and *A. wrightianum* in the upper part of the profile indicates wetter conditions than those at the base of the sequence.

Testate amoebae results have been quantitatively interpreted using transfer functions. For both the DWT and pH transfer functions between 79 and 99% of testate amoebae are included (average 92%). These lower values are primarily due to the absence of *Difflugia pulex* from both training sets. The TI-DWT results show a small decline in values from the lowermost sample to 104.5 cm of almost 2 cm (Fig. 6.4.9). From 104.5 cm there is an increase in values with a resumed increase after 102.5 cm. A peak of over 42 cm TI-DWT is reached at 101.5 cm. From 101.5 to 100.5 cm there is a marked decline of over 12 cm TI-DWT. Values are low from 100.5 to 99.5 cm and then increase to 98.5 cm by over 3 cm TI-DWT. Values gradually decline from 98.5 to 95.5 cm returning to 28 cm TI-DWT by the top of the profile. The tephra peak occurs immediately after the major decline between 101.5 and 100.5 cm, this change represents a significant shift to assumed wetter conditions. The TI-pH results show relatively stable values (4.5-4.6).
between the base of the profile and 102.5cm. Values decline by almost 0.2 to the 101.5cm sample. From 101.5 to 100.5cm there is a sharp increase in values of almost 0.4. From 100.5 to 98.5cm there is a gradual decline of around 0.2. In the uppermost four samples there is a gradual increase in values reaching over 4.7 by the top of the core. The tephra peak coincides with peak TI-pH values.

The macrofossil data show the peat in this profile to be heavily *Sphagnum* dominated (Fig. 6.4.9). From the base of the profile to 101.5cm there is a decline in *Sphagnum* content of around 9%, small increases in monocot content and more substantial increases in UOM content. From 101.5 to 98.5cm there is a small increase in *Sphagnum* content with a decline in UOM. The samples at 96.5 and 97.5cm are notable for a much higher monocot content (<28%); this increase is largely at the expense of *Sphagnum*. The uppermost sample marks a return to the earlier *Sphagnum* domination. The tephra peak at 100.5cm does not coincide with any marked changes in the profile.

**ST 12**

The humification results across the ST 12 tephra are shown in Fig. 6.4.11, both raw data and corrected values are shown. The corrected humification data show broadly constant values between the base of the profile and 13.75cm with a lower value at 14.25cm. Above 13.75cm there is a major decline reducing corrected transmission values to 44.6% by 12.25cm. This point marks a change to a rapid increase in values, increasing to 74% by 10.75cm. In the upper part of the section there is a return to greater stability with values broadly constant to 8.75cm and then a gradual increase to the top of the profile. From the base of the profile to 14.75cm and from 11.25cm to the top of the profile, the corrected humification values show very similar trends to the raw data. However in the center of this profile the raw data show a substantial increase in transmission values of around 10% while the corrected values show a decrease of around 25%. As is discussed later in this thesis, the trends in the corrected humification data appear to be primarily controlled by LOI rather than the measured humification values.

The testate amoebae results across the ST 12 tephra are shown in Fig. 6.4.12. The testate amoebae community in this site is relatively diverse with the greatest number of
species found of any of these profiles. From the base of the profile to 12.5 cm, the most abundant species is *Aflavum*, reaching over 35% of the total in the 12.75 cm sample. Several species are found consistently through much of this stage including *A.muscorum*, *E.ciliata*, *H.petricola*, *H.sphagni*, *H.elegans*, *H.papilio*, *N.militaris*, *N.tincta*, *P.acropodia*, *T.arcula* and *T.enchelys*. In the 12.75 and 13.25 cm samples there is notably less *T.arcula*, *N.tincta* and *H.petricola* and rather more *H.elegans* and *H.papilio* than in the samples below. 12.5 cm marks a distinct change in a few species; most notable is a reduction in the abundance of *Aflavum* from over 35% to around 8%. Coincident with this change is a reduced number of *H.papilio*, reduced occurrence of *H.elegans* and increased occurrence of *T.complanatum*. Above 12.5 cm there is a gradual increase in abundance of *Aflavum* returning to over 34% by the uppermost sample. This upper half of the section is also notable for the greater occurrence of *A.catinus*, *E.rotunda*, *N.lageniformis* and *T.complanatum*, these species were rare or absent in the lower half of the profile. A notable peak of *H.petricola* occurs in this upper half of the section at 9.25 cm reaching almost 30% of the total, largely at the expense of *Aflavum*. Although distinct changes are noted in some species, other moderately abundant species remain relatively constant through the profile including *N.militaris*, *T.enchelys* and *A.muscorum*.

The tephra peak in this profile occurs at the 12.25 cm sample. This coincides with several of the significant changes. Most striking are the reduced abundances of *Aflavum* and *H.papilio*. It is also after this point that several species (including *A.catinus*, *E.rotunda* and *T.complanatum*) are more abundant. These results suggest a fairly significant change coincident with tephra deposition. The major species declines are in two species known to be good indicators of wetter conditions. A qualitative interpretation of these data would therefore suggest a shift towards drier conditions.

Testate amoebae results have been quantitatively interpreted using transfer functions. For both the DWT and pH transfer functions between 98 and 100% of testate amoebae are included (average 99.2%). The TI-DWT results across the ST 12 tephra are shown in Fig.6.4.12, the data shows a high degree of variability. From 16.75 to 16.25 cm values decline by over 5 cm, values subsequently increase by over 2 cm to 15.25 cm depth. TI-DWT values are lower between 15.25 and 13.25 cm, with a trough centered on 14.25 cm. The sample at 12.75 cm has much the lowest inferred DWT of the sequence.
With values reduced to almost 25cm. The 12.25cm sample has a higher value (35cm) while the 11.75cm sample shows a return to lower values (under 30cm). From 11.75 to 10.75cm values increase to 36.5cm Tl-DWT, remaining high until the 9.75cm sample. Values fall again to 8.75cm, increase at 8.25cm, decline at 7.75 and increase again at 7.25cm. The tephra peak occurs in the 12.25cm sample, this coincides with a brief TI-DWT peak between the troughs at 12.75 cm and 11.75cm. The TI-pH results show a trend of increasing values from the base of the profile to 13.75cm. The sample at 13.25cm shows a lower TI-pH value (4.7) followed by a gradual increase to 11.75cm with values also high (>5.1) in the 11.25cm sample. Values decrease rapidly from 11.25 to 10.75cm (down to 4.8) and then more gradually to 9.25 (<4.6). From 9.25 to 7.25cm values fluctuate between 4.5 and over 4.8 with peaks at 8.75 and 7.75cm. The tephra peak at 12.25cm occurs in the middle of a trend of increasing TI-pH values.

Macrofossil data across the ST 12 tephra show the peat to be heavily Sphagnum dominated (Fig. 6.4.11). Throughout most of the core over 90% of the peat is composed of Sphagnum, monocots make up a further 5% and the remainder is made up by other components. The only major departure from this is between 12 and 13cm, at this point there is a distinct peak in monocots, increasing to over 20% of the total. The sample at 12.25cm also contains the greatest proportion of UOM of these samples. This monocot peak coincides with the tephra peak.

ST 24

The humification data for the ST 24 tephra are shown in Fig.6.4.13. The corrected transmission data show a rapid decline in values from the base of the profile to 26.75cm of over 8% (values at 27.25cm are marginally higher). At 27.25cm values increase to 54% before declining again to 49% at 25.75cm. From 25.75 to 20.25cm there is a broadly continuous increase in values to reach a peak of over 70%. Values decline slightly at 19.75cm and then increase in the uppermost sample. Between the base of the core and 24.75cm the raw data show a rather different pattern. In the raw data this region of the profile shows an initial increase reaching a double peak at 26.75cm and 25.75cm. The
Fig. 6.4.13 Summary diagram for the ST 24 tephra. Details as for ST 12.

Fig. 6.4.15 Summary diagram for the ST 36 tephra. Details as for ST 12.

Fig. 6.4.17 Summary diagram for the MP 10 tephra. Details as for ST 12.

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discrepancy between these data sets suggests that the humification correction is primarily forced by LOI.

The testate amoebae diagram for the ST 24 tephra is shown in Fig. 6.4.14. These data do not show the single species dominance that is a feature of many of the other sites. At the base of the profile the most abundant species is *P. gracilis*, there is also abundant *T. arcula* and *P. acropodia*. From the base of the profile to 27.75 cm there is a gradual increase in *P. gracilis* to over 39%. The 27.75 cm sample is also marked by a notably low abundance of *T. arcula* and a reduced abundance of *P. acropodia*. From 27.25 cm *A. flavum* is present in greater abundance. From 27.25 to 23.25 cm there is a gradual increase in the abundance of *A. flavum* reaching an initial peak of over 26%; there is a marked loss of *P. gracilis* over this region. This region of the core contains the greatest abundances of several of the more minor species (*C. aerophilosa, D. diffugia* and *E. Euglypha* species). From 23.25 to 20.75 cm there is reduced abundance of *A. flavum*, this is also the region of the core in which *T. arcula* and *A. catinus* are most abundant. From 20.75 cm to the upper sample there is a resumed increase in *A. flavum* abundance reaching a peak in the upper sample of over 45%. Overall, the results from this section show less variability than in other sections. Although marked changes are present in *P. gracilis* and *A. flavum*, changes in other major species (*T. arcula, P. acropodia, N. tintec, N. militaris* and *H. papilio*) are fairly limited. The tephra profile at this site is more complicated than in the other sections. LOI indicates a double tephra layer with peaks at 25.75 and 26.75 cm. There are few major changes around these points. The gradual increase in *A. flavum* through the central section of this profile starts around 25.75 cm. This is broadly coincident with the upper tephra peak but this is not a distinct relationship. Both tephra peaks occur somewhat above the start of the decline in *P. gracilis*.

Testate amoebae results have been quantitatively interpreted using transfer functions. For the DWT transfer function between 93 and 100% of testate amoebae are included (average 98%), for the pH transfer function between 92 and 100% are included (average 97.8%). The TI-DWT results across the ST 24 tephra are shown in Fig. 6.4.13; the results show a great deal of variability. The lowest three data points show an upward trend followed by a marked trough at 27.25 cm (37.5 cm). From this point there is a generally upward trend to 23.75 cm, interrupted by troughs at 26.25, 25.25 and 24.25 cm.
Fig. 6.4.14 Testate amoebae diagram for the ST 24 tephra. Details as for CHP 33.

G) ST 24

Fig. 6.4.16 Testate amoebae diagram for the ST 36 tephra. Details as for CHP 33.

H) ST 36

Fig. 6.4.18 Testate amoebae diagram for the MP 10 tephra. Details as for CHP 33.

I) MP 10
Following the peak at 23.75cm (57cm TI-DWT) there are two lower values at 23.25 and 22.75cm followed by two higher values at 22.25 and 21.75cm. The following stage of the section shows a high degree of variability with peaks at 20.75 and 19.75cm and troughs at 21.25, 20.25 and 19.25cm. The final sample at 19.25cm has a particularly low value of 38cm TI-DWT. The double tephra peak corresponds with minor peaks of TI-DWT (i.e. wetter conditions) within a more general phase of increasing values. The TI-pH data show more consistency than the TI-DWT results. From the base of the profile to 27.25cm the results show a trend of increasing TI-pH reaching a peak of almost 6. This peak is the highest TI-pH value shown in any profile and suggests conditions which are only slightly acidic. From this peak there is a consistent trend of declining values to 21.75cm, reaching 4.3. From 21.75 to 20.75cm values increase marginally and fluctuate around 4.5 for the remainder of the profile. The double tephra peak occurs within the zone of gradually declining TI-pH values; both samples have fractionally lower values than the samples on either side of them.

The Macrofossil results show a single major change in peat composition through the profile (Fig. 6.4.13). In the lower two samples the peat is monocot dominated (>50%) with substantial amounts of UOM (>15%) and smaller amounts of Sphagnum. From 27.75cm there is a rapid increase in Sphagnum abundance, increasing to 66% by 26.75cm. This increase in Sphagnum is largely at the expense of monocots, which decline in abundance to around 15% by 26.25cm. From this point to the top of the profile there is a gradual increase in Sphagnum abundance to around 80% and a general decrease in UOM abundance. The double tephra peaks at 25.75 and 26.75cm occur immediately above the phase of increasing Sphagnum abundance, there are no further abrupt changes above the tephra peaks.

ST 36

The humification results across ST 36 are shown in Fig. 6.4.15. The corrected transmission results show a high degree of consistency in the lower part of the core. Below 35.75cm values fluctuate between 44 and 48% but show no overall trend. From 35.75 to 34.25cm there is a marked reduction in values of 13% to 34.2%. From 34.25 to
32.75 cm values increase, returning to their former levels. From 32.75 cm to the top of the profile there is a gradual decline in values. The raw data show a different pattern with an increasing trend from 37.25 cm reaching a peak at 34.25 cm and declining to 33.25 cm with stable values to the top of the profile. The difference between these two plots again suggests that the humification correction factor is primarily controlled by LOI values.

The testate amoebae results across the ST 36 tephra are shown in Fig. 6.4.16. Three species (*A. cafinus*, *H. sphagni* and *T. arcula*) in varying proportions account for most of the counted tests in this profile. In the three lowest samples, *H. sphagni* is the most abundant species showing a trend of increasing values. Other significant species include *A. flavum*, *A. cafinus*, *H. papilio*, *T. arcula* and to a lesser extent *A. stenostoma*. From around 35 cm a few changes are present including an increase in extent of *T. arcula* (16% at 35.25 cm increasing to 32% at 34.75 cm) and reduced occurrence of *A. flavum*. In the 34.25 and 34.75 cm samples there is noticeably less *A. cafinus* than previously (reduced to under 8%). *H. sphagni* reaches its highest values of the profile at 34.25 cm, over 51% of the total count. At around 33 cm there is a significant loss of *H. sphagni*, decreasing from 42% at 33.25 cm to under 8% at 32.75 cm with no tests found in the uppermost samples at 31.25 cm and 31.75 cm. Corresponding with this decline in *H. papilio* is an initial increase in *T. arcula* (particularly in the 32.25 cm sample) followed by an increase in *A. cafinus*, which reaches its highest levels in the upper two samples. Also in this upper portion of the profile there is a brief stage of *P. acropodia* with values as high as 8% in the upper four samples. Overall this profile shows a great deal of variability with several significant changes in major species. The tephra peak in this core is at 34.25 cm. This is near to the start of a period of gradual increase in *A. cafinus* and around 1 cm below the decline in *H. sphagni* and increase in *P. acropodia*. These changes are not all exactly coincident with the tephra peak; although a relationship with tephra deposition cannot be ruled out it seems unlikely.

Testate amoebae results have been quantitatively interpreted using transfer functions. For both the DWT and pH transfer functions between 96 and 100% of testate amoebae are included (average 99.3%). The TI-DWT results across ST 36 show a distinct trend of increasing values through the profile. From the base of the section to 35.25 cm values are relatively constant, mostly around 25-30 cm TI-DWT. From 35.25 cm values
increase to a peak at 34.75cm (40cm TI-DWT) before declining again at 34.25cm (>31cm TI-DWT). From 34.25 to 32.25cm values increase to reach a peak of almost 57cm TI-DWT. The 31.75cm sample has a lower value but the 31.25cm sample is higher again. The tephra peak occurs within the zone of increasing values, in the sample above the minor peak at 34.75cm. The TI-pH results show values fluctuating around pH 4 between the base of the profile and 34.25cm. From this point results show a general trend of declining values with an initial trough at 33.75cm and then a resumed decline from 33.25cm to 31.75cm, reaching <3.1. The final sample has a somewhat higher value of 3.4. The tephra peak at 34.75cm follows a small increase in values from the sample below.

The macrofossil results for the ST 36 tephra show little overall change (Fig.6.4.15). Through most of the profile, the peat is monocot dominated (around 60%) with significant amounts of UOM (around 30%) and some Ericales (5-10%). While there is significant variation in these components, there is no overall trend. *Sphagnum* is present in small quantities but is infrequent after 36.25cm. The tephra peak at 34.25cm does not coincide with any major changes in the macrofossils. It is notable that the subsequent sample has the highest UOM content of profile, however this is probably within the associated analytical errors.

**MP 10**

The humification data across the MP 10 tephra are shown in Fig.6.4.17. From the base of the profile to 11.25cm the corrected values show a decreasing trend, interrupted by a particularly low value at 12.25cm. From 11.25 to 10.75cm there is a reduction in values of over 15%. Above this there is a trend of increasing values to an initial peak at 8.75cm, following this there is a small decline and then a resumed increasing trend to the top of the profile. The raw data show a different pattern in the center of the profile. From the base of the section to 11.25cm the pattern is similar with the exception of the trough at 12.25cm which is not present in the uncorrected data. From 11.25 to 9.75cm the raw
data show substantially higher values, reaching a peak at 10.75cm. At the time of this peak the corrected data show a sharp trough.

The testate amoebae data across the MP 10 tephra layer are shown in Fig.6.4.18. At the base of the sequence the community is dominated by *T. arcula* and *A. catinus* with smaller quantities of *B. indica*, *D. cf pristis* and *N. tineta*. From 14.5 to 12.5cm there is a gradual decrease in *B. indica* abundance (from 19 to 5% abundance) and an increase in *N. tineta* abundance (from 8 to 20% abundance). Some changes in testate amoebae community occur around 11cm with a substantial decline in *T. arcula* (from 18 to 7%), a decline in *B. indica* and the first substantial numbers of *A. wrightianum*. Also broadly coincident is an increase in *D. cf pristis*, abundances in the 10.5 and 11.5cm samples are the highest of the section (up to 38%). The sample at 9.5cm is notable for a higher abundance of *A. catinus* and rather low abundance of *D. cf pristis* and *A. wrightianum*. Through the uppermost four samples there is a gradual increase in *T. arcula* and a decline in *D. cf pristis*. In the uppermost four samples there is the first substantial occurrence of *P. spinosa* and in the uppermost three samples, the first substantial occurrence of *T. complanatum*. The tephra peak in this section occurs at 10.5cm. This coincides with the peak of *D. cf pristis* and occurs somewhat after the decline in *A. catinus* and the decline in *T. arcula*. These changes are not all entirely synchronous with the tephra peak and any tephra impact is unclear.

For both the DWT and pH transfer functions between 60 and 86% of testate amoebae are included (average 77.7%). These low values are largely due to the abundance of *Difflugia cf. pristis*, which is not present in either of the training sets. A reduced count of 100 tests was used across this tephra layer; it is therefore possible that the testate amoebae community may be less-well characterized. Transfer function results must therefore be treated with caution. The TI-DWT results across the MP 10 tephra are shown in Fig.6.4.17. Results show an increase in values from the base of the profile to 13.5cm. From 13.5cm there is a consistent downwards trend to 10.5cm, values fall from almost 69 to under 53cm TI-DWT. From 10.5cm there is a brief peak to 9.5cm (>57cm TI-DWT) followed by a decline to 7.5cm (50cm TI-DWT). In the upper two samples there is an increase in values to >61cm TI-DWT. The tephra peak at 10.5cm lies in a trough between the major decline from 13.5cm and the minor peak at 9.5cm. The TI-pH
results show a substantial increase in values from 14.5 to 10.5 cm, rising from around 3 to >3.6. The sample at 9.5 cm shows a much lower TI-pH (3.1) however values increase again in the 8.5 cm sample (3.9). Values remain around 3.9 to the top of the profile. The tephra peak at 10.5 cm coincides with a peak between the initial increase and the trough at 9.5 cm.

The macrofossil results across the MP 10 tephra again show the peat to be *Sphagnum* dominated. Through most of the profile *Sphagnum* exceeds 80% (Fig.6.4.17). From the base of the profile to 9.5 cm the peat is consistently composed of around 90% *Sphagnum*, 4% monocots and 6% UOM. At 8.5 cm there is a significant increase in UOM to around 16%, reducing *Sphagnum* to under 75%, there are also rather more monocots in this sample (over 8%). The subsequent sample at 7.5 cm shows much greater *Sphagnum* abundance with monocots and UOM reduced to under 3% each. The 6.5 cm sample is more similar to that at 8.5 cm with 80% *Sphagnum*, 10% monocots and 7% UOM. This sample also has the most abundant Ericales of the profile (3%). The uppermost sample has over 95% *Sphagnum*, around 4% monocots and under 1% UOM. The tephra peak at 10.5 cm does not coincide with any major changes in the macrofossil record. The more variable phase in the upper half of the core occurs slightly above the tephra.

**MP 27**

The humification data across the MP 27 tephra are shown in Fig.6.4.19. The corrected data show little change from the base of the profile to 29.75 cm, fluctuating around 52-54%. From this point values decline, initially gradually and then more rapidly to a low-point at 27.75 and 27.25 cm. Following this, values increase rapidly, to 62% by 26.25 cm. Values remain around 60% from here to the top of the profile. The values towards the top of the profile are rather higher than those towards the base. The raw data show similar trends from 30.25 cm to the base of the profile and from 25.75 cm to the top of the profile. The raw data show a major peak in transmission values in the 27.25 and 27.75 cm samples, coinciding with the trough in corrected values.

Fig.6.4.20 shows testate amoebae data across the MP 27 tephra layer. This testate amoebae diagram shows a great deal of variability in composition. The sample at the base
Fig. 6.4.19 Summary diagram for the MP 27 tephra. Details as for ST 12.

Fig. 6.4.21 Summary diagram for the MP 39 tephra. Details as for ST 12.
of the sequence is somewhat different from those above. This sample at 31.5cm has high abundance of *T. arcula* (29%) with significant amounts of *A. catinus* (19%) and notable amounts of *D. cf pristis*, *H. papilio*, *N. tincta* and *A. wrightianum*. The sample above (30.5cm) contains a markedly different community, most distinct is the much greater abundance of *D. cf pristis* (>66%). This sample also contains markedly less *T. arcula* and very little *H. papilio*. From 30.5cm to 28.5 there is a decline in *D. cf pristis* abundance to 43% and an increase in *T. arcula* to 18%. No testate amoebae data were obtained for the 27.5cm sample due to the massive abundance of tephra shards. The sample directly above the tephra layer at 26.5cm contains a lot more *T. arcula* (41%) and less *D. cf pristis* (27%) than below. This sample at 26.5cm contains relatively little *A. catinus* (3%) but marks the start of a trend of increasing values to reach 37% by the uppermost sample at 22.5cm. Above 27.5cm, *A. muscorum* is present more frequently and in greater abundances. In the uppermost three samples at 22.5, 23.5 and 24.5cm *H. papilio* is present in greater quantities than previously in the section, *N. militaris* is also present in greater quantities in the 23.5 and 24.5cm samples. Above 24cm there is a sharp decline in abundance of *D. cf pristis*, percentages in the upper two samples are much reduced compared to the two samples below. These low values of *D. cf pristis* coincide with the highest abundances of *A. catinus*. The tephra layer at 27.5cm coincides with some changes in the palaeoecological data including a dramatic increase in *T. arcula*, a decline in *D. cf pristis* and the start of a gradual increase in *A. catinus*. The absence of data from the 27.5cm sample means that these changes may be more gradual than suggested by the diagram. The data do suggest that some of these changes might be associated with tephra deposition although some of changes could represent the continuation of pre-existing trends.

For both the DWT and pH transfer functions between 31 and 91% of testate amoebae are included (average 66.8%). These values are extremely low due to the abundance of *Difflugia cf. pristis* and to a lesser extent *Difflugia pulex*. These species are not included in the transfer function and as such ecological information is lost and quantitative interpretation is based on only a reduced number of testate amoebae. Results are still presented as the majority of species are still included but these must be treated with a great deal of caution. TI-DWT results for the MP 27 tephra are shown in Fig.
Fig. 6.4.20 Testate amoebae diagram for the MP 27 tephra. Details as for CHP 33.

J) MP 27

Fig. 6.4.22 Testate amoebae diagram for the MP 39 tephra. Details as for CHP 33.

K) MP 39
6.4.19. At the base of the profile there is a sharp change between the sample at 31.5cm (55.5cm TI-DWT) and the sample at 30.5cm (39cm TI-DWT). From 30.5cm to 28.5cm there is an increase in TI-DWT of around 15cm. The sample at 27.5cm has no data, however the sample above this at 26.5cm has a much higher value at almost 72cm TI-DWT. From 26.5cm there is a decline in values down to 52cm TI-DWT at 22.5cm. The tephra layer lies in the middle of a trend of increasing TI-DWT values. TI-pH results show a similar pattern to TI-DWT (Fig.6.4.19). Values decline from the uppermost sample to 30.5cm. From 30.5cm values increase up to the tephra layer. Above the tephra layer at 26.5cm, TI-DWT is marginally higher (>3.9). From 26.5cm TI-DWT values decline consistently, down to 3.1 by 22.5cm. The tephra layer lies near to the peak of TI-pH values.

The macrofossil results across the MP 27 tephra are shown in Fig.6.4.19. As can be seen, the composition of the peat is highly variable. From the base of the profile to 31.5cm there is a sharp decline in *Sphagnum* down to around 15%. From 30.5cm *Sphagnum* increases reaching a peak of 70% at 28.5cm. *Sphagnum* percentages fall sharply between 27.5 and 26.5cm down to around 30%. Percentages increase again from 25.5cm, returning to around 70%. The monocot abundances largely mirror this variability in *Sphagnum* with a maximum value of 78% reached at 30.5cm and a minimum value of 20% at 24.5cm. UOM is most abundant in the lower two samples (over 10%) before declining up the profile; ericales is present in small quantities through most of the profile. The tephra layer at 27-28cm occurs immediately below the second major shift from *Sphagnum* to monocots.

**MP 39**

The humification data across the MP 39 tephra are shown in Fig.6.4.21. From the base of the profile to 39.75cm values fluctuate around 50-60%. From 39.75cm, values decline by around 30% to 39.25cm. From 39.25cm values recover, returning to over 60% by 38.25cm. From 38.25cm values remain broadly constant between 60 and 70% to the top of the profile. The raw data shows similar trends above 38.25cm and below 41.25cm
but is characterized by a marked peak at 39.25cm corresponding with the trough in the corrected data.

The testate amoebae data for the MP 39 tephra are shown in Fig.6.4.22. The palaeoecological data shows some variability in the testate amoebae community with dominance changing between *A. catinus*, *D. cf pristis* and *T. arcula*. At the base of the profile the most abundant species is *D. cf pristis* (over 44%). Other species include *A. catinus*, *N. tincta* and *T. arcula* in smaller quantities. From 43.5 to 40.5cm there is a rapid decline in *D. cf pristis* from 44% to 8% and a corresponding increase in *T. arcula* from 8% to 56%. The 40.5cm sample is notable for the very low abundance of *H. papilio*, *N. militaris*, *N. tincta*, *P. acropodia* and *P. spinosa*. From 41cm there is an increase in *A. catinus* from 12% to 48% at 38.5cm, corresponding with this is a decline in *T. arcula*, *Amphitrema wrightianum* is also less abundant above 40cm. The 37.5cm sample is notable for a drop in abundance of *A. catinus* and increase in *T. arcula*. In the uppermost three samples from 36.5 to 34.5cm there is a decline in *A. catinus* and a small increase in *T. arcula*. These three samples are also notable for greater quantities of *H. papilio* and *N. tincta*. The tephra peak occurs at the 39.5cm sample in this profile. Few notable changes occur around this point. Although *T. arcula* decreases and *A. catinus* increases across the tephra layer, these changes both seem to be occurring at least 1cm below the tephra layer.

Testate amoebae results have been quantitatively interpreted using transfer functions. For both the DWT and pH transfer functions between 55 and 94% of testate amoebae are included (average 84.9%). These low values are primarily due to the abundance of *Difflugia cf pristis* and somewhat undermine quantitative interpretation. Results are presented as the majority of species and individuals are still included. The TI-DWT results across tephra MP 39 show fluctuating values (Fig.6.4.21). From the base of the profile to 40.5cm there is a trend of increasing values reaching almost 70cm TI-DWT. From 40.5, values decline down to 50cm TI-DWT by 38.5cm. The sample at 37.5cm shows substantially higher TI-DWT (66cm), values decline further to 36.5cm, down to around 37cm TI-DWT. TI-DWT increases in the upper three samples, values returning to over 52cm. The tephra peak occurs in a phase of declining TI-DWT values. The TI-pH results show a general decline from the base of the profile to 38.5cm, reaching under 2.8.
Values increase to a brief peak at 37.5 cm (>3.3) before declining to almost 2.7 at 36.5 cm. These values are extremely low and suggest highly acidic conditions. From 36.5 cm values increase to almost 3.4 by 34.5 cm. The tephra peak occurs within the phase of declining values and does not appear to be associated with any distinct changes.

The macrofossil data across the MP 39 tephra shows the peat to have a mixed composition (Fig. 6.4.21). *Sphagnum* is the most abundant component, making up at least 60% of the peat. Monocots compose around 5% of the peat although this is generally greater towards the base of the section. UOM ranges between around 15 and 30%, a notable peak is present at 37.5 cm, Ericales are of limited extent through the profile. The tephra peak at 39.5 cm does not coincide with any marked changes in macrofossil composition.

### 6.4.2 Tephras without full testate amoebae data

In some of the investigated profiles testate amoebae concentrations were too low to allow counting. Data for these profiles are described in the following section. In some of the profiles, the major testate amoebae taxa have been identified by counting the tests in one slide per sample. These results are presented as Tables 6.4.2-6.4.4.

**ECR 32**

The humification profile across tephra ECR32 is shown in Fig. 6.4.23. At the base of the section, values fluctuate greatly up to the 35.75 cm sample. Above this there is a gradual increase to reach a peak at 33.75 cm (24.3%). Following this peak there is a consistent decline in values to 32.25 cm (20.6%). Above this, there is a significant increase in transmission values, increasing by 4% to a peak at 30.25 cm. To the top of the section there are fluctuating values but with no overall trend. The tephra peak occurs at 32-33 cm, this depth coincides with the change from a distinct decrease in values to a trend of rapidly increasing values.

The macrofossil results across this tephra layer show that the peat is of mixed composition (Fig. 6.4.23). Throughout the sequence, *Sphagnum* is generally around 25%, monocots around 50%, and UOM around 25% with minor proportions of other
Fig. 6.4.23 Summary results for the ECR 32 tephra showing tephra concentration, raw (dotted) and corrected humification values and macrofossil peat components. See text for full details of methods.

Fig. 6.4.24 Summary diagram for the SPM 26 tephra. Details as for ECR 32.

Fig. 6.4.25 Summary diagram for the LNA 465 tephra. Details as for ECR 32.

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components. There are few distinct trends overall. It is notable that the uppermost sample contains a greater proportion of Sphagnum and less UOM than previous samples. The sample at 32.5cm is particularly notable for a very high proportion of Ericales (14%), a component which is rare (<2%) through the rest of the profile. This peak coincides with the tephra peak at 32.5cm.

SPM 26

The humification results for the SPM 26 layer (Fig. 6.4.24) shows a general increase in values from 30.25 to 27.25cm reaching a peak of 27.68%. Following this there is a small decline in values from 27.25 to 26.25cm. Following this small decline is a resumed increase to 32.4% at 25.25cm. Above this peak there is little overall trend to the top of the sequence, values fluctuating around 30-40%. The tephra layer in this section reaches a peak at 26-27cm. This point coincides with the small decline and then resumed increase in transmission values. The strong upward trend of transmission values makes it somewhat difficult to determine any tephra impacts upon this profile.

The macrofossil results (Fig. 6.4.24) show that at the base of the core the peat is predominantly composed of Sphagnum remains. In the 33.5cm sample the peat is composed of around 80% Sphagnum, 7% monocots, 7% UOM and 6% Ericales. The subsequent sample at 32cm shows significantly less Sphagnum (45%) with more monocots (22%), UOM (16%) and Ericales (18%). The 30cm sample shows a return to earlier Sphagnum dominated composition. The six upper samples are composed of around 85% Sphagnum around 10% monocots with a few percent each of UOM and Ericales. The tephra peak at 26.5cm does not coincide with any marked changes in the macrofossil data. Testate amoebae were not sufficiently abundant to count in this profile, however the major species have been recorded in Table 6.4.2. These results show the most abundant taxa to be N. tincta, A. catinus and T. arcula. A community of this type can be taken to represent a relatively dry peat surface.
Table 6.4.2 Testate amoebae found in samples across the SPM 26 tephra.

<table>
<thead>
<tr>
<th>Depth range (cm)</th>
<th>Testate amoebae</th>
</tr>
</thead>
<tbody>
<tr>
<td>19-21</td>
<td><em>N. tincta</em>, <em>T. arcula</em>, <em>H. papilio</em> (2), <em>N. militaris</em>, <em>A. catinus</em></td>
</tr>
<tr>
<td>21-23</td>
<td><em>N. tincta</em>, <em>H. papilio</em> (2), <em>N. militaris</em></td>
</tr>
<tr>
<td>23-25</td>
<td><em>T. arcula</em>, <em>N. militaris</em> (2), <em>N. lageniformis</em>, <em>A. catinus</em> (2)</td>
</tr>
<tr>
<td>25-27</td>
<td><em>N. militaris</em> (2), <em>H. papilio</em> (2), <em>A. catinus</em>, <em>Hyalosphenia subflava</em>, <em>N. tincta</em></td>
</tr>
<tr>
<td>27-29</td>
<td><em>H. papilio</em> (2), <em>T. arcula</em>, <em>N. militaris</em>, <em>A. flavum</em> (2), <em>A. catinus</em></td>
</tr>
<tr>
<td>29-31</td>
<td><em>H. papilio</em> (2), <em>A. catinus</em> (2), <em>T. arcula</em>, <em>A. muscorum</em>, <em>A. flavum</em></td>
</tr>
<tr>
<td>31-33</td>
<td><em>T. arcula</em> (3), <em>N. tincta</em>, <em>N. militaris</em></td>
</tr>
<tr>
<td>33-35</td>
<td><em>H. papilio</em>, <em>A. muscorum</em>, <em>D. cf. pristis</em></td>
</tr>
</tbody>
</table>

LNA 465

The humification results for the LNA 465 tephra show an overall trend of declining transmission values (Fig. 6.4.25). In the lower part of the section, values are quite consistent between 470.75 and 468.75 cm. Above this there is a rapid increase to a peak at 468.25 cm (23.4%), this peak is followed by a decreasing trend which continues until 466.25 cm. From here, values begin to stabilize although there is a further decline at 465.25 cm. Transmission values remain low (between 10.5 and 14%) for the remainder of the profile. The tephra profile for this site shows a peak concentration at 466-467 cm. The humification data do not show any distinct changes at this point, values are relatively stable.

The macrofossil data across the LNA 465 tephra does not show any distinct changes (Fig. 6.4.25). Through the profile the results show the peat is composed of around 40% monocots and 60% UOM. There is rather more *Sphagnum* present between 460 and 464 cm, Ericales are most abundant at the base of the profile. The tephra peak at 465.5 cm coincides with a small peak in UOM but this is not a major change.
Fig. 6.4.26 Summary diagram for the MTR 32 tephra. Details as for ECR 32.

Fig. 6.4.27 Summary diagram for the MTR 146 tephra. Details as for ECR 32.

Fig. 6.4.28 Summary diagram for the MTR 190 tephra. Details as for ECR 32.

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MTR 32

The humification results for the MTR 32 tephra are shown in Fig. 6.4.26. From 37.75 to 34.25 cm there is no overall humification trend; values fluctuate around 20%. A minor peak is reached at 34.25 cm of 21.95% immediately below a significant decline down to 15.61% transmission at 33.25 cm. From 33.25 cm there is a trend of increasing values, this is particularly pronounced between 32.25 and 32.75 cm, transmission values increasing to 26%. This sharp increase is followed by a period of greater stability and a secondary peak of 27.28% at 30.75 cm. Above this peak there is a gradual decline to 28.25 cm, followed by increasing values for the uppermost two data-points. The tephra concentration peaks at 32-33 cm, this depth is coincident with the sharp increase in values and lies immediately above the lower values around 33.25 cm.

The macrofossil results across the MTR 32 tephra do not show any major changes in peat composition (Fig. 6.4.26). Through the profile the peat is composed of around 60-70% monocots, around 30% UOM and a few percent Ericales with *Sphagnum* present in some samples. The tephra peak at 32.5 cm does not coincide with any major changes although it is notable that the highest value of Ericales through the profile (>9%) occurs within the tephra peak at 32.25 cm. Testate amoebae were not sufficiently abundant to count, the main species are shown in Table 6.4.3. These results suggest the most abundant species are *Tarcula* and *Acatinus* indicating a generally dry peat surface.

MTR 146

The humification profile across tephra MTR146 (Fig. 6.4.27) exhibits more stability in values than many of the other profiles. From 151.75 cm to 147.75 cm values remain consistently between 24.5% and 26.5% with the exception of a minor peak at 149.75 cm. A significant peak is reached (147.25 cm) with values falling from 28.1% to 23.9% up to 146.75 cm. A second peak is reached at 146.25 cm (27.7%) before a drop to 147.75 cm. From 145.75 to 142.25 cm transmission values remain stable with little change until the uppermost two points, which have a lower transmission than those below them. The tephra layer in this site peaks at 146-147 cm. This coincides with the upper of the two
mid-core peaks and the trough between these two peaks. This event is one of the most significant changes in this profile but is very short lived and is of smaller magnitude than the changes noted in other profiles.

Table 6.4.3 Testate amoebae found in samples across the MTR 32 tephra.

<table>
<thead>
<tr>
<th>Depth range (cm)</th>
<th>Testate amoebae</th>
</tr>
</thead>
<tbody>
<tr>
<td>26-27</td>
<td><em>H. papilio</em> (3), <em>B. indica</em> (2)</td>
</tr>
<tr>
<td>27-28</td>
<td><em>H. papilio</em>, <em>P. acropodia</em></td>
</tr>
<tr>
<td>28-29</td>
<td><em>H. papilio</em>, <em>E. rotunda</em></td>
</tr>
<tr>
<td>29-30</td>
<td><em>A. catinus</em> (3), <em>P. acropodia</em></td>
</tr>
<tr>
<td>30-31</td>
<td><em>T. arcula</em> (3), <em>A. catinus</em> (2)</td>
</tr>
<tr>
<td>31-32</td>
<td><em>B. indica</em>, <em>T. arcula</em>, <em>A. catinus</em></td>
</tr>
<tr>
<td>32-33</td>
<td><em>T. arcula</em> (2), <em>A. catinus</em></td>
</tr>
<tr>
<td>33-34</td>
<td><em>P. acropodia</em>, <em>D. pulex</em></td>
</tr>
<tr>
<td>34-35</td>
<td><em>D. pulex</em></td>
</tr>
<tr>
<td>35-36</td>
<td><em>A. catinus</em>, <em>T. arcula</em></td>
</tr>
<tr>
<td>36-37</td>
<td><em>T. arcula</em>, <em>D. pulex</em></td>
</tr>
<tr>
<td>37-38</td>
<td><em>T. arcula</em>, <em>P. acropodia</em></td>
</tr>
<tr>
<td>38-39</td>
<td><em>A. catinus</em> (2)</td>
</tr>
</tbody>
</table>

The MTR 146 macrofossil profile shows the peat is of mixed composition (Fig. 6.4.27). From the base of the profile to 146.5cm the peat is composed of around 20% *Spahgnum*, 35% monocots and 45% UOM. From 146.5 to 142.5cm there is an increasing amount of *Spahgnum*, reaching over 50% of the total, although values decline in the uppermost samples. This *Spahgnum* increase coincides with a decline in UOM and starts at the same time as the tephra peak.

MTR 190

The humification data across the MTR 190 tephra is shown in Fig. 6.4.28. The data show a marked decline in transmission values through the lower half of the profile. From 195.75 to 194.25cm there is little overall trend, however from 194.25cm there is a marked decline. Transmission decreases from 24.4% at 194.25cm to 15% at 190.75cm. From this point, values begin to recover to earlier levels reaching 21.5% at 188.25cm. This is followed by a further gradual decline with values reaching 16.4% at 185.75cm; the final sample has a greater transmission value. The tephra concentration peaks at 190-
191cm, this coincides with the trough at 190.75cm and the shift from declining values to increasing values.

The MTR 190 macrofossil diagram shows a fairly high degree of overall variability (Fig.6.4.28). From the base of the profile to 195.75cm there is relatively little Sphagnum, the peat is monocot dominated (around 50-60%) with high proportions of UOM (around 20%) and relatively high Ericales (10-15%). From 195.25 to 192.25cm there is substantially more Sphagnum (around 40-50%) with the increase largely at the expense of UOM. From 190.75 to 191.75cm there is reduced Sphagnum (around 20-30%) with greater UOM and Ericales. From 190.25cm to the surface there is again more Sphagnum with variable amounts of UOM, monocots and Ericales. The tephra peak at 190.5cm coincides with a shift to a more Sphagnum-dominated composition with a corresponding decrease in UOM. Testate amoebae were relatively rare in this profile. Table 6.4.4 shows A.flavum to be the most abundant species; this is generally a good indicator of a wet mire surface.

Table 6.4.4. Testate amoebae found in samples across the MTR 190 tephra.

<table>
<thead>
<tr>
<th>Depth range (cm)</th>
<th>Testate amoebae</th>
</tr>
</thead>
<tbody>
<tr>
<td>183-184</td>
<td>A.flavum (3), A.muscorum</td>
</tr>
<tr>
<td>184-185</td>
<td>A.flavum (3)</td>
</tr>
<tr>
<td>185-186</td>
<td>C.aculeata, H.elegans, A.flavum, A.seminulum</td>
</tr>
<tr>
<td>186-187</td>
<td>Habrotrochoa, H.papilio</td>
</tr>
<tr>
<td>187-188</td>
<td>A.catinus (2), A.flavum (4), H.papilio (2)</td>
</tr>
<tr>
<td>188-189</td>
<td>C.aculeata, A.flavum (5)</td>
</tr>
<tr>
<td>189-190</td>
<td>A.flavum (4), A.muscorum</td>
</tr>
<tr>
<td>190-191</td>
<td>A.flavum (3), C.aculeata</td>
</tr>
<tr>
<td>191-192</td>
<td>A.flavum (2), T.arcula</td>
</tr>
<tr>
<td>192-193</td>
<td>A.muscorum (2), T.arcula (2), C.aculeata, A.flavum</td>
</tr>
<tr>
<td>193-194</td>
<td>A.flavum (4), A.catinus</td>
</tr>
<tr>
<td>194-195</td>
<td>A.flavum (2)</td>
</tr>
<tr>
<td>195-196</td>
<td>T.arcula, A.flavum</td>
</tr>
<tr>
<td>196-197</td>
<td>A.flavum (2), A.muscorum</td>
</tr>
<tr>
<td>197-198</td>
<td>A.flavum (2), A.catinus</td>
</tr>
</tbody>
</table>

ST 68

The humification results across the ST 68 tephra are shown in Fig.6.4.29. The corrected values show broad stability around 40-42% between the base of the profile and 70.75cm and from 67.75cm to the top of the profile. From 70.75cm to 69.25cm values
Fig. 6.4.29 Summary diagram for the ST 68 tephra. Details as for ECR 32 with the exception of tephra concentration, results here show loss on ignition, the trough represents the tephra peak.

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decline to a trough at 25.5% before recovering to previous levels. The raw data show an inverse pattern with values constant around 52-54% at the top and base of the profile but reaching a peak of 75% transmission at 69.25cm. This peak in raw values and trough in corrected values coincides with the LOI trough representing the tephra layer.

The macrofossil results across this tephra are shown in Fig. 6.4.29. The diagram shows a mixed but relatively constant peat composition through much of the profile. From the base of the profile to 69.25cm the peat is composed of around 15% *Sphagnum*, 55% monocots, 25% UOM and 5% Ericales. Between 69.25cm and 66.75cm there is a distinct change with markedly more *Sphagnum* reaching a peak of 47%. This increase in *Sphagnum* is largely at the expense of UOM with only a minor reduction in monocot abundance. From 66.75cm to the top of the profile the peat composition is similar to that at the base of the profile. It is noticeable that there is less Ericales in this upper half of the profile.
6.4.3 Statistical analyses.

The testate amoebae data across eleven of the tephra layers have been examined using statistical techniques. Initially data sets were investigated using zonation analysis. These techniques were developed for the division of long biostratigraphic sequences into sub-units to allow interpretation and comparisons between sites. Four techniques were tested- CONSLINK, CONISS, SPLITLSQ and SPLITINF. If the zone boundaries assigned by these techniques coincide with the location of a tephra peak this provides evidence for a change coincident with tephra deposition and circumstantial evidence for a volcanic impact. Results are shown in Table 6.4.5. In general CONSLINK did not produce a single zone boundary at the most significant level, results are therefore of little use for this purpose. For the other three methods it can be seen that for six of the data-sets the most significant zone boundary determined by at least one of these methods coincides with the tephra layer. However for two of these, MP 27 and CHP 33 this coincidence is only noted by one of the methods. For four of the data-sets (ECR 100, ECR 162, LNA 100 and ST 12) all methods show a major zone boundary immediately adjacent to the tephra peak. This provides convincing evidence for palaeoecological change coincident with tephra deposition. In three of the data-sets (ECR 162, LNA 100 and ST 12) the division is between the sample containing the tephra peak and the sample directly below, for the ECR 100 data set the division is between the tephra peak sample and that directly above. For a further two data-sets (MP 10 and MP 39) the analyses suggest that the most significant change in the sequence occurs one sample removed from the tephra peak, but this cannot be taken as evidence for an impact. Overall these results provide reasonable evidence for an impact associated with tephra deposition. 14 out of the 36 zone boundaries identified in Table 6.4.5 lie adjacent to tephra peaks, this proportion is more than double what would be expected simply by chance.

Zonation analyses can provide circumstantial evidence for change associated with tephra deposition. However, they do not provide a rigorous test of the hypothesis that changes are due to a volcanic impact. An alternative methodology is to use RDA with a variable to represent a volcanic impact and variance partitioning to separate the impact of non-volcanic factors. This has been carried out for all testate amoebae data sets; results
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are shown in Table 6.4.6. Initially redundancy analyses were carried out simply using the volcanic impact model as the sole explanatory variable. Monte Carlo permutation tests showed the relationship to testate amoebae data to be significant in four data-sets: CHP 33, LNA 100, ST 12 and ST 24. The volcanic impact variable explained between 33 and 64% of the variance and the relationships were just significant at the $P<0.05$ level. However these analyses do not provide a good tests of the volcanic impact hypothesis due to the possibility of other confounding factors. Most significant of these is time and therefore the possibility for pre-existing change to be mistaken for a volcanic impact.

When depth (used as a surrogate for time) is partialled out only two of the relationships remain significant- for data sets LNA 100 and ST 12. The reasons for this are readily determined by taking the example of the ST 24 data set. In this profile there are long-term changes occurring throughout the sequence (a general increase in *A.flavum* and *N.tincta*, a decrease in *P.gracilis*) that are not clearly related to the tephra peak. As the tephra peak occurs towards the base of the sequence the ‘Volcanic’ variable is actually very similar to simply depth (=time). Partialling out the depth component to leave solely the volcanic impact greatly reduces the proportion of variance explained and the remaining relationship is not significant.

Table 6.4.5. Zonation analysis of testate amoebae data across tephra layers using four methods (see text and Gordon & Birks 1972 for details). Zone boundaries highlighted in bold lie immediately adjacent to the tephra peak. Samples are labelled as depth of upper surface therefore a division of 30-31 lies between the samples from 30-31cm and 31-32cm.

<table>
<thead>
<tr>
<th>Method</th>
<th>CHP33</th>
<th>ECR100</th>
<th>ECR162</th>
<th>LNA39</th>
<th>LNA100</th>
<th>ST12</th>
<th>ST24</th>
<th>ST36</th>
<th>MP10</th>
<th>MP27*</th>
<th>MP39</th>
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<tbody>
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<td>CONSLINK</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>CONISS</td>
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<td>99-100</td>
<td>162-163</td>
<td>43-44</td>
<td>100-101</td>
<td>12-12.5</td>
<td>23-23.5</td>
<td>32.5-33</td>
<td>11-12</td>
<td>23-24</td>
<td>41-42</td>
</tr>
<tr>
<td>SPLITLSQ</td>
<td>35-36</td>
<td>99-100</td>
<td>162-163</td>
<td>34-35</td>
<td>100-101</td>
<td>12-12.5</td>
<td>24.5-25</td>
<td>32.5-33</td>
<td>11-12</td>
<td>26-28</td>
<td>40-41</td>
</tr>
<tr>
<td>SPLITINF</td>
<td>32-33</td>
<td>99-100</td>
<td>162-163</td>
<td>35-36</td>
<td>100-101</td>
<td>12-12.5</td>
<td>24.5-25</td>
<td>32.5-33</td>
<td>11-12</td>
<td>23-24</td>
<td>40-41</td>
</tr>
</tbody>
</table>

* For the MP27 tephra no testate amoebae data was obtained from the 27-28cm sample, this sample was therefore excluded from analysis.

Identification of volcanic impacts may also be complicated by the impact of change in macrofossils or humification. To investigate these relationships, these factors were partialled out both with and without depth as a covariable. When simply the macrofossil and humification data are partialled out the relationships are significant for
three data-sets; ECR 162, LNA 100 and ST 12. When time is also included as a co-
variable only the relationships in ST 12 and LNA 100 remain significant. By this strictest
definition the 'Volcanic' variable explains 16% of the variance for LNA 100 and 15% for
ST 12, the relationship for ST 12 is moderately significant (P=0.02), the relationship for
LNA 100 is highly significant (P=0.002). When considered independently the
macrofossil data explain a moderate amount of variance and humification explains a
small proportion of variance. These relationships are all non-significant with the
exception of humification in ST 12, however due to the problems of measuring
humification across large tephra layers, this relationship is probably just showing a
relationship with the tephra layer (Section 7.4.2).

Overall the statistical analyses show evidence for a variable response. The
zonation analyses show evidence for impacts associated with four tephra layers, this is
broadly supported by qualitative examination of the data. However the RDAs show that
only two of these relationships are consistent with a volcanic impact as modelled here.
Table 6.4.6. Results of RDA and variance partitioning exercise for testate amoebae data. Results are shown as percentage variance explained by each combination of explanatory variables and covariables. Values shown in brackets are not significant at P<0.05 level, values in bold are significant with the P values shown in superscript. Unexplained variance is variance not explained by all four explanatory variables.

<table>
<thead>
<tr>
<th>Source of variance</th>
<th>Explanatory variables</th>
<th>Covariables</th>
<th>CHP 33</th>
<th>ECR 100</th>
<th>ECR 162</th>
<th>LNA 39</th>
<th>LNA 100</th>
<th>ST 12</th>
<th>ST 24</th>
<th>ST 36</th>
<th>MP 10</th>
<th>MP 27</th>
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<tbody>
<tr>
<td>Volcanic impacts</td>
<td>Volcanic</td>
<td></td>
<td>47.0^a</td>
<td>48.1</td>
<td>57.2</td>
<td>34.5</td>
<td>64.0^a</td>
<td>33.0^a</td>
<td>34.0^a</td>
<td>42.0</td>
<td>46.0</td>
<td>46.0</td>
<td>32.0</td>
</tr>
<tr>
<td>Volcanic impacts independent of time</td>
<td>Volcanic</td>
<td>Depth</td>
<td>21.5</td>
<td>26.0</td>
<td>26.0</td>
<td>23.5</td>
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<td>14.0</td>
<td>24.0</td>
<td>37.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Volcanic impacts independent of plant and humification change</td>
<td>Volcanic</td>
<td>Humification, Macrofossils</td>
<td>19.5</td>
<td>20.5</td>
<td>30.0</td>
<td>12.0</td>
<td>27.0</td>
<td>26.0</td>
<td>8.0</td>
<td>24.0</td>
<td>42.0</td>
<td>29.0</td>
<td>23.0</td>
</tr>
<tr>
<td>Volcanic impacts independent of plant, humification change and time</td>
<td>Volcanic</td>
<td>Humification, Macrofossils, Depth</td>
<td>19.5</td>
<td>13.0</td>
<td>19.0</td>
<td>8.0</td>
<td>16.0</td>
<td>15.0</td>
<td>8.0</td>
<td>10.0</td>
<td>8.0</td>
<td>11.0</td>
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</tr>
<tr>
<td>Independent plant affects</td>
<td>Macrofossils</td>
<td>Humification, Volcanic, Depth</td>
<td>10.0</td>
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<td>27.0</td>
<td>28.0</td>
<td>18.0</td>
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<td>13.0</td>
<td>23.0</td>
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</tr>
<tr>
<td>Independent humification affects</td>
<td>Humification</td>
<td>Macrofossils, Volcanic, Depth</td>
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<td>4.0</td>
<td>6.0</td>
<td>5.0</td>
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<td>3.0</td>
<td>5.0</td>
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</tr>
<tr>
<td>Unexplained variance</td>
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<td></td>
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<td>15.0</td>
<td>5.0</td>
<td>13.0</td>
<td>4.0</td>
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<td>33.0</td>
<td>27.0</td>
<td>21.0</td>
<td>7.0</td>
<td>23.0</td>
</tr>
</tbody>
</table>
CHPTER 7. DISCUSSION

7.1 TEPHRA DISCUSSION

The tephra results reveal several important findings about the tephrochronology and volcanic history of Alaska. These findings have wider implications for volcanic hazard assessment and tephrochronology in the region. The results are considered region by region.

7.1.1 Southeast Alaska

The SPM 26, ECR 32 and LNA 39 tephras are geochemically very similar to the late Holocene White River Ash (WRA). Given the similarity in depth and approximate age it is highly probable that the CHP 33 and MTR 32 tephras also correlate with these layers. A date from the CHP 33 tephra places this tephra around 280-320 cal.BP (1630-1670 AD). This is significantly too young to be the younger White River Ash eruption (Eastern Lobe), which has been dated to around 1147BP (Clague et al. 1995). No more recent eruptions are recorded from Mt. Churchill, the most probable source of this tephra (Table 7.1.1). The only volcano in the Wrangell-St. Elias range to have recorded eruptions within the last 1000 years is Mt. Wrangell. Several eruptions have been suggested including events around 1784, 1884-5 and 1900 although not all of these are certain (Richter et al. 1995a). No eruptions are recorded within the probable age range of these tephras. Although Mt. Wrangell was one of the volcanoes initially suggested as a possible source of the WRA (Dawson 1888, Richter et al. 1995b) this now seems extremely unlikely (Lerbekmo & Campbell 1969, Richter et al. 1995a&b, Clague et al. 1995) and geochemical similarity is improbable. Therefore the most likely source of this tephra is a previously unrecognized eruption of the WRA source (most probably Mt. Churchill) around 1650AD. Given the lack of historical records for the region, the limited tephrochronology and absence of previous micro-tephra research it is extremely probable that some eruptions could have gone unrecorded, even in comparatively recent times. This eruption must have been a moderately large event to produce significant micro-
tephra layers at this distance. I propose the name ‘Lena tephra’ for this layer following the convention of naming previously unknown tephras after the site in which they were first located.

Table 7.1.1 Holocene eruptive activity of selected Alaskan volcanoes. Source: the Smithsonian global volcanism program website www.volcano.si.edu. Only confirmed eruptions are included.

<table>
<thead>
<tr>
<th></th>
<th>Spurr</th>
<th>Augustine</th>
<th>Redoubt</th>
<th>Iliamna</th>
<th>Hayes</th>
<th>Churchill</th>
<th>Wrangell</th>
<th>Aniakchak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2ka BP</td>
<td>c.890AD, c.510AD, c.230AD</td>
<td>c.110AD</td>
<td>c.700AD c.60AD</td>
<td>c.190AD</td>
<td>1963AD, 1966AD, c.1650AD, c.1540AD, c.1200AD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-3ka BP</td>
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<td>c.1550BC, c.1850BC</td>
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<td>c.4550BC</td>
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<td>9-10ka BP</td>
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Three lower tephras (MTR 146, LNA 100 and CHP 184) are also very similar in composition to the WRA. The LNA 100 layer has been dated to 1375-1290BP (575-660 AD). Given the age and very high degree of geochemical similarity this tephra is probably the younger White River Ash (Eastern Lobe) tephra (Table 6.1.6A). The age of this eruption has been discussed by Clague et al. (1995). Ten radiocarbon dates were presented mostly on wood preserved in the tephra layers, the calibrated age ranges span from 791 to 1416BP. The authors opted for a weighted mean of the four ‘best’ dates to
assign an age estimate of 1147BP (803 AD) to the tephra. The radiocarbon date obtained here is considerably older than this averaged date. The mid-point of the age range for SUERC-5913 is older than the mid-point of all ten dates presented by Clague et al. (1995) although there is some overlap in age-range with eight of these dates. Although it is possible that the LNA 100 tephra is a different tephra from the same source the geochemical similarity and dating overlap means this is unlikely. I consider that the SUERC-5913 date is superior to the previously presented dates and provides the best age estimate for the White River Ash. The date in this study was obtained by AMS; the dates previously presented have all been conventional radiometric dates. AMS allows the use of smaller sample sizes and therefore only material directly associated with the tephra to be dated. This is reflected by the greater precision in this study, this date has a precision of +/- 28 compared to precisions of between 60 and 140 years for the dates presented by Clague et al. (1995). The date in this study also has an advantage in terms of the material dated. The previous studies used wood preserved in proximal volcanic deposits, this wood did not have the bark intact and therefore the surface may not exactly have represented the time of the eruption. The Sphagnum leaves used in this study are an optimal material for radiocarbon dating (Mauquoy et al. 2004) and are directly associated with the tephra peak. Overall I feel that it is justified to adjust the recognized age of this tephra and propose that the actual age of the event is around 150 years older than previously recognized, c.1375-1290BP. This improved age estimate may have important implications for the use of the tephra layer as an isochrone (Robinson & Moore 1999) and to investigate the environmental impact of the eruption in climatic records.

The MTR 146 tephra is similar in composition to the LNA 100 layer and the Lena tephra, however this layer is considerably older. The tephra has not been directly dated but the outline age-depth model suggests an age of around 6300BP. This is considerably older than both the WRA eruptions. No pre-White River Ash eruptions of Mt Churchill are recorded. Eruptions in the Holocene may have occurred from several volcanoes in the Wrangell-St.Elias range including Mts. Sanford and Gordon, although these eruptions are undated (www.volcano.si.edu). Given the geochemical similarity to the WRA a previously unknown eruption of the same source (Mt.Churchill) seems most likely.
The CHP 184 tephra is also similar in composition to the WRA. The site only has one radiocarbon date which is considered reliable and that is from near the surface. It is therefore difficult to estimate the age of this tephra. The appearance of the peat and to some extent the humification plot suggests that this depth may be early in the Holocene. The geochemistry strongly suggests that this tephra is from the WRA-source. Without improved dating it is impossible to determine whether the tephra is from either WRA eruption, the probable mid-Holocene eruption identified at Mount Riley, a previously unidentified eruption or even conceivably the c.300BP Lena tephra eruption.

Three other tephras in southeast Alaska are probably from more distant sources. The geochemistry of the ECR 162 tephra show a high degree of similarity to tephra from Aniakchak. The tephra is dated to 5300-5030BP, this is considerably older than all dates on the most recent caldera-forming eruption (Begét et al. 1992). This eruption is likely to have been relatively large in order to deposit this tephra layer at such a distance (1400Km). Miller & Smith (1987) described evidence for an older eruption of Aniakchak (referred to as Aniakchak I) dated to sometime between 4400 and 10,000BP (Neal et al. 2001). VanderHoek & Myron (2004) estimated the age of Aniakchak I to c.8200BP rather older than ECR 162. The Smithsonian database also dates an eruption at 2550BC +/-500 (c.4500BP) somewhat later than the date of ECR 162. An eruption of Aniakchak is the most likely source of this tephra. However, Miller & Smith (1987) also described evidence for a caldera-forming eruption of Black Peak with an uncalibrated date of 4470 +/-200, this is very close to the uncalibrated date of ECR 162 at 4485 +/-30BP. Other unpublished dates also show good overlap with ECR 162 (Tina Neal, USGS, personal communication). Similarity with Black Peak tephra was limited (SCs~0.8) but, in contrast to Aniakchak, there are very few comparison data-sets (Riehle et al. 1999). The proximity of the two volcanoes and apparent similarity in age means that an eruption of Black Peak cannot be ruled out. However the most likely source of the tephra is an Aniakchak eruption which may be that termed Aniakchak I but could be a separate event.

The geochemistry of the ECR 100 tephra suggests that the most likely source is an eruption of Mt. St. Augustine, although the data are limited (Table 6.1.6B). The age-depth model places this tephra at around 2840 cal.BP. The literature and the Smithsonian database do not record any Augustine eruptions prior to c.200AD. Given the frequency of
eruptions over the last 1000 years it seems very likely that there are unrecognized Holocene eruptions prior to this date. The most likely source of ECR 100 is an Augustine eruption around this age.

There is limited geochemical evidence for the MTR 190 tephra although the most likely source is an eruption of Mt. Redoubt. The age-depth model dates the tephra to around 8660 BP. The nearest recorded eruption to this date has an uncorrected radiocarbon date of 5780 +/- 150 BC (c. 7730 BP). This eruption is the ‘best guess’ for the source of the tephra but there is considerable uncertainty in this.

Overall these results provide considerable new knowledge about the tephrochronology of southeast Alaska. Firstly the results demonstrate the applicability of micro-tephrochronology in Alaska. These results demonstrate that microscopic methods can reveal the presence of Holocene tephra layers in regions for which none were previously known. These tephras may be useful markers in palaeoenvironmental studies in the region. Perhaps the most interesting find is the widespread Lena tephra. This tephra is found in all the southeast sites and may be a very useful isochrone. The tephra indicates a previously unrecognized eruption of the WRA-source. The LNA 100 tephra shows the presence of the WRA (Eastern Lobe) in southeast Alaska, considerably extending the southern limit of this tephra layer (Robinson 2001). The radiocarbon date on this layer probably provides the best age estimate for this eruption and demonstrates that it is older than previously thought. These results together with the MTR 146 and CHP 184 tephras indicate that the WRA-source (Mt. Churchill) has had much more Holocene activity than previously recognized. Given the scale of some of these eruptions and their impacts on human populations (Moodie et al. 1992, Workman 1979) this finding has serious implications for volcano-hazard assessment in the region.

The presence of tephras which may originate from Mts. St. Augustine, Redoubt and Aniakchak indicates that even tephras from distant volcanoes may be transported to southeast Alaska. The presence of these specific tephras indicate that these may have been particularly large events. The ECR 162 tephra is probably from Aniakchak and either indicates that the Aniakchak (I) event may have been later than previously believed or that there was an unrecognized mid-Holocene eruption. None of the southeast Alaskan tephras appear to be from Mt. Edgecumbe, the only volcano in southeast Alaska.
Similarity coefficients with geochemical data from the Younger Dryas age Edgecumbe tephra are low (SC<0.85). Although there are no comparison data from the mid-Holocene eruptions the geochemical composition would be expected to be broadly similar. These results therefore suggest that the mid-Holocene eruptions were either very minor, or that tephra plumes were not directed north towards these sites.

7.1.2 South-central Alaska

The tephrochronology of the sites in south-central Alaska is rather more complicated. The MP 10 tephra shows a great deal of similarity to tephra from the 1883 Augustine eruption. Given the limited similarity to older Augustine tephras this eruption seems the most likely source. There is no external dating evidence from this site, however 1883 does seem a reasonable age for this depth. The MP 27 tephra is similar in composition to tephra at Skilak Lake (Begét et al. 1994) attributed to Crater Peak (Mt. Spurr) and dated to c.300BP. Crater peak is the only volcano in south-central Alaska known to produce widespread mafic tephras such as this layer. Given the accumulation rate suggested by the upper tephra layer c.300BP would seem a reasonable age for this depth. The lowest tephra at the Moose Pass site is the MP 39 tephra, this layer is similar in composition to MP 27 (SC=0.96). The mafic composition and similarity to MP 27 strongly suggest the source as Crater Peak, however the age of the eruption is unclear. Begét et al. (1994) document a Crater Peak tephra which they do not date but which is older than 500BP, however this bears limited similarity to MP 39 (Table 6.1.8B). The Smithsonian database (Table 7.1.1) only lists one eruption between 5000BP and 1953AD, at 1650AD +/-50 which presumably correlates with that found at Skilak Lake c.300BP. This therefore suggests that one of MP 27 and MP 39 is a previously unrecognized layer. Given the probable accumulation rate of the site and the probable 1883 date of MP 10 it seems much more probable that MP 27 is this 1650AD +/-50 eruption than MP 39. This indicates that MP 39 is a new isochrone, the age of the tephra is unknown but based on the probable accumulation rate is likely to be c.430BP.

In the Sterling site there is more uncertainty about the source of the tephras. The ST 12 tephra shows the greatest geochemical similarity to Augustine tephras. The highest
similarity is to the c.500BP layer at Skilak Lake with only limited similarity to the 1883 tephra (Table 6.1.8C). The outline age-depth model indicates that this layer has an age of around 250BP. Comparison to the Smithsonian database shows that the nearest Augustine eruption to this date is an eruption dated to 1650AD. This eruption may be the source of this tephra although 20th century observations show a high frequency of eruptive activity so it is probable there were unrecognized eruptions in the past. The ST 24 tephra shows the greatest degree of similarity to the Katmai-Novarupta 1912 tephra (Table 6.1.8C). The dating suggests an approximate age for this layer of c.500BP. Given this dating and probable accumulation rates it is extremely unlikely that this tephra could be Katmai-Novarupta 1912, no older Katmai eruptions are recorded. The source of this tephra is therefore uncertain. The similarity to Katmai may suggest one of the adjacent volcanoes as the source; there is also a degree of geochemical similarity to Augustine tephra. The ST 36 tephra shows a fairly limited degree of similarity to other tephras compared although Augustine tephras are the most similar (Table 6.1.8C). The radiocarbon date suggests an age of around 760BP. The Smithsonian database (Table 7.1.1) shows an eruption at c.1200AD, which would agree with this date. Overall there is uncertainty over the source of this tephra although this c.1200AD Augustine eruption is a likely candidate. The source of the ST 68 tephra may be Mount Hayes, although the age of this eruption is uncertain. If this tephra layer is from Hayes it would be the first documented Hayes tephra on the Kenai Peninsula, although the tephra also bears a degree of similarity to Augustine tephra. Extrapolation from the radiocarbon date would suggest an age for this tephra of around 1440BP. There are no Hayes tephras recorded between c.1200AD and c.1550BC. If this date were correct it would therefore indicate an unrecorded eruption. However there is some uncertainty in this due to the limited dating evidence and possible accumulation rate change. It is conceivable that the layer may be from one of the large Hayes eruptions in the second millennia BC (Bégét et al. 1991b).

These results have some interesting implications for tephrochronology in the Kenai region. Although some tephras have a distinct origin and are relatively well known (MP 10, MP 27), many more are not. The MP 39 tephra is in all probability from Crater Peak (Mount Spurr) and probably represents a previously unrecognized eruption. The sources of many of the Sterling tephras are unknown but in all probability represent
eruptions of Mt. Augustine and possibly one eruption of Mt. Hayes. These tephras represent new discoveries for the region and it is possible that some may be from previously unrecognized eruptions. If the ST 68 layer is from Hayes then this would be particularly interesting suggesting a large eruption. Further geochemical study including trace elements and improved dating would be required to establish the source of these tephras. These layers provide new tephrochronological markers that are probably widely present in peatlands across the region.

7.1.3 Western and Interior Alaska.

The Akhlun Mountains and Espenburg tephras show a high degree of similarity to proximal Aniakchak tephra and previous studies of distal Aniakchak tephra. Given the size of the layers and their coincidence with the distribution of tephra from the c.3500 eruption it is extremely probable that this is the source of the layer. The presence of the tephra therefore confirms this distribution but does not extend it.

No tephras have previously been encountered in interior Alaska in the region of the Dot Lake B site; this tephra is therefore a new isochrone for the region. The source of the tephra has not been adequately determined and the site is undated; at present it therefore adds little to our knowledge of tephra distribution in Alaska.

7.1.4 Review of the methodology

The tephra studies here have been generally effective at both locating tephra layers and identifying their sources. However, some specific problems have been encountered. Perhaps the most distinct issue is the lack of comparison data. Alaskan volcanoes have produced thousands (perhaps tens of thousands) of Holocene tephra layers. However, the limited tephra research in Alaska means that only a small minority of these tephras have geochemical data. Therefore when trying to identify unknown tephras, particularly in distal regions, it can be difficult to make correlations and to identify a probable source. Making these correlations can also be difficult due to differences in microprobe performance. Hunt & Hill (1996) have demonstrated that
instrumental differences can make a distinct difference to results, as shown by the apparent differences in microprobe performance between the two machines in this study. It is therefore possible that some of the difficulties in making correlations may have been due to difference in probe performance.

Similarity Coefficients have both advantages and disadvantages for correlating tephra layers. The method is computationally simple and allows the comparison of numerous data-sets. In this study over 3000 individual correlations were made. This number of comparisons would be unfeasible by graphical approaches or qualitative data comparison. Very few tephra layers in this study had a SC>0.95 with tephra layers from more than one source. Tephra identified using SCs showed a high degree of similarity when compared by graphical approaches. This indicates that the method is relatively effective at identifying tephra to source eruptions. However, interpretation of the results is more complicated when maximum SC<0.95. For instance for the DLB 11 layer, tephra from four sources produce SCs between 0.90 and 0.94, it is therefore impossible to determine the source. Similarity Coefficients have a generally poor ability to differentiate between similar layers, in particularly to differentiate tephra from different eruptions of the same volcano. For instance, the MTR 190 tephra gives SCs>0.95 with three different Redoubt tephras.

The SC method disregards potentially useful information about the geochemistry of the tephra layers. In this study and most others, oxides with a low abundance are excluded from the calculation due to their higher percentage errors. This exclusion is necessary but means that potentially useful information is disregarded. The method also weights each oxide equally; this may result in loss of information as small but significant differences in one oxide may be masked by the gross similarity of others, this has been illustrated by the microwave digestion experiment (Appendix I).

The cluster analysis used in this study has been effective at illustrating the internal structure in the tephra data and identifying internal correlations. The success of the method may justify its more widespread use. The graphical approaches have also been of value for identifying tephra to their source. Graphical approaches are limited in the number of oxides and data-sets which can be represented at a time. It would be unfeasible to compare numerous tephra by graphical approaches. Plots can only present up to three
separate oxides at a time meaning that it is not possible for the complete data-sets to be compared and a sub-set of oxides must be (subjectively) selected. Graphical approaches are also limited as only data averages have been published in most Alaskan tephra studies so comparison of data-structures is not possible. In making tephra correlations the most effective approach may to be use multiple techniques including graphical and statistical approaches.

7.1.5 Summary

These tephra results show several important features of Alaskan tephrochronology. The micro-tephra findings illustrate the potential of microscopic methods to extend tephra distributions. Previously unrecognized tephra layers are located indicating previously unknown eruptions of Mt. Churchill and Mt Spurr, probably Mt. St. Augustine and possibly Mt. Redoubt, Mt. Hayes and Aniakchak caldera. These findings may necessitate reassessment of volcano hazard assessment, particularly for Mt. Churchill. The dating evidence indicates that the White River Ash (eastern lobe) may be older than previously thought and that the Aniakchak I eruption could be younger than thought.

**Key Findings**

- Micro-tephras can extend the distribution of tephra layers in Alaska
- Several, potentially important and previously unidentified eruptions are identified
- The White River Ash (eastern lobe) may be significantly older than previously thought
7.2 FULL CORE HUMIFICATION- PEATLANDS & PALAEOCLIMATE

The full core humification records presented previously can be used to investigate the Holocene climate of southeast Alaska and the role of climate in peatland development. Although in Europe it seems clear that climate plays a primary role in peatland development this cannot necessarily be assumed for North America given the significant differences in peatland structure, species and climatic regimes. A recent study from eastern North America concluded that climate played only a minor role in peatland development (Muller et al. 2003). Several European studies have used multiple sites to investigate climatic controls on peatland development. If palaeoecological records from hydrologically separate mires show agreement in pattern this provides strong support for climatic forcing. The simplicity and rapidity of humification analysis make it particularly suitable for this purpose (see section 5.4 for details of the method).

The full core humification records from these sites do not agree entirely, however several key features are replicated between them (Fig.6.3.2). From the beginning of the Holocene to c.6000BP there is less variability in values and very little agreement between profiles. A drier phase from c.6000 to c.8000BP in the Mount Riley site is not shown by the other profiles. In the Mount Riley and Spaulding Meadows sites there is a distinct dry phase from c.4000 to c.5000BP. In the Eaglecrest site values are also low around this point, however a more distinct dry phase is dated to 3200-3700. This later dry phase is more similar to the pattern in Mount Riley and Spaulding Meadows, given the limitations of the age-depth model it is possible that this phase does correlate. In the Eaglecrest, Mount Riley and Spaulding Meadows sites a very distinct wet shift is present around 3-4000BP, this shift is somewhat later in the Eaglecrest site than in the others. This wet shift is followed by a wet phase lasting to around 2000BP. Around 2000BP there is a dry shift in the Eaglecrest, Mount Riley and Spaulding Meadows sites; this change is less pronounced at Spaulding Meadows than at the others. Following this dry shift the Mount Riley and Eaglecrest sites show increasing values reaching a minor peak around 800-1400BP showing a slight return to wetter conditions. The Spaulding Meadows site also shows a minor peak around 1000BP but this is of a smaller magnitude. Following the minor peaks in Mount Riley and Eaglecrest values decline followed by a rapid decrease.
to the top of the profile. This rapid increase probably represents the transition into the acrotelm and therefore may not be recording a climatic change. The Spaulding Meadows site shows a sharp drop in values around 1000BP. This might correlate with the more minor declines at similar ages in the Mount Riley and Eaglecrest sites.

The Chilkoot Pond site has poor dating control; on the basis of this age-depth model there is very little agreement with the other sites. However it seems likely that the base of this profile is actually considerably older than indicated here, probably dating to the early Holocene. This profile shows a distinctive period of lower values from 80-90cm followed by a marked wet shift and a period of higher stable values to 50cm. It is tempting to assign this pattern to the very similar change seen in the other profiles from approximately 2-5000BP. However without better dating it is impossible to be sure of this.

Overall these profiles do show several common features. These features are quite distinctive and suggest that the peatlands are undergoing common allogenic forcing. It therefore seems probable that climate does have a major role in peatland development in southeast Alaska. There is however some difference between the profiles, particularly in shorter-term variability. This probably represents differences in the sensitivity of the sites and possibly local climatic differences. The disparity in inferred ages of some of the changes is more likely to be due to the limited nature of the age-depth models and the large sampling interval as opposed to actual climatic differences. There is less commonality towards the base of the profiles. As noted in previous studies this is probably as the sites were minerotrophic in the early Holocene and became more climatically sensitive as they approached ombrotrophy.

Several distinct climatic changes are suggested by the results. These changes can be compared to previous palaeoclimatic studies to investigate the extent to which the records agree with those at other sites and by other methods. Table 7.2.1 shows a summary of the major palaeoecological and palaeoclimatic changes recorded in 18 recent studies using various methods from Alaska and northern Canada. The results can also be compared to the large body of peatland palaeoclimate research from northwest Europe to see the extent to which these changes may be global or northern hemisphere climate shifts. A summary of this data is presented by Hughes et al. (2000) and has been updated
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<td>300 mm</td>
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Table 7.2: Major vegetation, environmental, and climate changes recorded in selected previous paleoecological studies from Alaska.
by Ellershaw (2004) and Barber et al. (2003). A distinct dry phase in the mid-Holocene is one of the most pronounced features of the profiles; this is dated to around 4-5000BP in the Mount Riley and Spaulding Meadows profiles but is dated earlier (3-4000BP) at Eaglecrest. This phase could well correlate with a warm period from 4000-4600BP noted by Anderson et al. (2001) in oxygen isotope ratios from central Alaska. A major wet shift in the profiles is dated to around 4000BP onwards. A shift to wetter and/or cooler conditions has been found in several studies around this time including a peat accumulation change in western Canada (Yu et al. 2003), pollen, ostracod and geochemical changes in lake sediments from southwest Alaska (Hu et al. 1996, 1998) and possible glacier advances (Calkin 1988). Wet shifts of a similar age have also been noted in many European peat studies (Aaby 1976, Nilssen & Vorren 1991, Tipping 1995, Haslam 1987, Hughes et al. 2000, Barber et al. 2003). The humification profiles suggest a dry-shift around 2000BP, this change is not widely found elsewhere. The humification records suggest a relatively minor wet shift around 1000BP followed by drier conditions around 3-500BP. This drier phase could correlate to a warmer period around 2-400BP noted by Anderson et al. (2001). Wet shifts around 1000-1200BP have been indicated in several European peat-based records (Haslam 1987, Blackford & Chambers 1991, 1995, Barber et al. 1994, Chambers et al. 1997, Mauquoy & Barber 1999, Ellis & Tallis 2000, Barber et al. 2003). The higher values at the top of the profiles are probably due to the presence of little decomposed acrotelm peat.

Overall it seems that several of the changes in these humification profiles could be reflected in other studies, however the limited age-depth models and coarse sampling intervals mean that these tentative correlations must be treated with caution. Nevertheless the evidence for a climatic deterioration around 4000BP seems relatively convincing and appears to be reflected in both European peat-based records and palaeoclimatic records from Alaska, potentially suggesting a climate change spanning the northern Hemisphere.

<table>
<thead>
<tr>
<th>Key Findings</th>
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<td>- Peatland development in Alaska seems to be controlled by climate</td>
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<td>- These results provide the first outline peatland palaeoclimatic record from Alaska and western North America</td>
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<td>- Some of the inferred climatic changes show apparent agreement with the results of other studies</td>
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7.3 VOLCANIC IMPACTS AND MODE OF RESPONSE

The key theme of this thesis is to investigate volcanic impacts on peatlands and the modes of these impacts. Two working hypotheses have been proposed which can be assessed against the null hypothesis that there are no volcanic impact on peatlands:

A) Volcanic impacts occur through the direct impact of volcanic products on the peatland ecosystem.

B) Volcanic impacts on climate produce impacts on the peatland through a changed mire surface wetness.

In order to assess the extent to which the observed impacts support these suggestions it is necessary to consider the manner in which these impacts might be represented in the palaeoecological record.

The possible impacts of a volcanic-induced climate change are the easiest to consider. A volcanic impact on climate would produce a reduction in solar insolation and therefore a climatic cooling. The duration of this climatic cooling is uncertain with modern studies suggesting a cooler climate for one or two years. For very large eruptions or when there are multiple eruptions within a short time-span impacts may last decades (Zielinski 2000). A shorter-term impact on precipitation may also occur due to the presence of volcanic aerosols in the troposphere. The full-core humification results demonstrate that the palaeoecological record from peatlands in Alaska is controlled by climate. The cooler, wetter climate caused by a volcanic impact would lead to reduced evapotranspiration and therefore an increase in mire surface wetness (decreased DWT) in ombrotrophic peatlands. In minerotrophic peatlands the response may be more complicated due to the input of groundwater although an increased mire surface wetness is also probable here.

If this increased surface wetness lasts for a decade or more it is likely to be detectable in the palaeoecological record. In the macrofossil record an increased surface wetness would be shown as a relative shift towards Sphagnum species and away from UOM and Ericales. Depending on the pre-existing composition of the peat, monocotyledons may either increase (if previously UOM dominant) or decrease (if
Sphagnum becomes dominant). In the humification record an increased surface wetness would mean that peat takes less time to reach the catotelm and therefore is less decomposed. This would mean less organic acid production leading to the alkali extract having a greater transmission value. Increased mire surface wetness would be reflected in the testate amoebae analysis as a change in species composition. In general, hydrophilic species such as Amphitrema flavum and Amphitrema wrightianum would be expected to expand their distribution and xerophilic species such as Bullinularia indica and Assulina muscorum to contract their distribution, the exact change would depend on the pre-existing condition of the site. This change would be reflected as decreased TI-DWT values across the tephra layer. As TI-DWT and TI-pH co-vary this could also be shown as an increase in TI-pH.

It is more complicated to identify how a direct volcanic impact on peatlands would be represented in the palaeoecological record. The literature review suggested several possible mechanisms:

A) Hydrological change due to tephra deposition
B) An impact of volcanic gas and acids with or without a change in peatland acidity
C) A chemical impact of tephra through leachates or adsorbed compounds
D) A physical impact of tephra

It is possible that tephra deposition might change the hydrology of the peatland, perhaps resulting in water being trapped near the peat surface (Crowley et al. 1994). An impact of this nature would be represented very similarly to a volcanic induced climatic deterioration i.e. an increase in Sphagnum at the expense of monocotyledons, Ericales, and UOM, a shift towards hydrophilic testate amoebae and therefore reduced TI-DWT and a reduced humification (i.e. increased transmission).

The ecological experiment and the literature review provide good evidence for the potentially severe impacts of volcanic acids on peatland plants. In the ecological experiments impacts were severe causing death of all plants at higher applications. At lower applications there was limited evidence for species-dependent affects with
bryophytes preferentially killed. Contemporary ecological studies and the historical record indicate the sensitivity of plants to volcanic gases as well as volcanic acid precipitation. The sensitivity of bryophytes, and particularly *Sphagnum* to acid deposition has been demonstrated in contemporary studies (Ferguson et al. 1978, 1980). An impact of this nature might therefore be shown in the macrofossil record as a loss of *Sphagnum*. If severe impacts on plants occur then there might be a hiatus or reduction in peat growth which might be detectable in an age-depth plot. If the peat growth is reduced then there may be a peak in humification (i.e. trough in % transmission) and UOM abundance as it takes plant matter longer to reach the catotelm. A severe impact on plants might be expected to have a knock-on impact on testate amoebae, however the way in which individual species would react (and therefore the impact on TI-DWT and TI-pH) is difficult to predict. The ecological experiment failed to show any detectable response to the acidity impacts on plants in testate amoebae communities, although this may have been due to the limitations of the experiment. The death of plants could potentially reduce transpiration leading to increased surface wetness and impacts as discussed above (Charman 2002).

It is also possible that volcanic acid deposition would affect peatland acidity. In modern ecological studies, peatland pH has been shown to be directly related to precipitation pH (Skiba et al. 1989, Proctor & Maltby 1998). This therefore suggests that volcanic acid deposition might lead to peatland acidification which could be detected as a decreased TI-pH. However in the ecological experiment there was only a very short-term decrease in pH and the long-term trend was more consistent with an increase in pH. This trend was also found in the control plot and therefore was possibly due to unrelated external factors. An increase in peat pH is a conceivable impact of a volcanic acidity input, perhaps due to reduced polyuronic acid production, leaching of organic acids or the release of metal cations from tephra leachates (Hodder et al. 1991). Such an impact would show the reverse effect, represented as an increase in TI-pH. If organic acids were lost by leaching this could potentially show in the palaeoecological record as reduced humification (increased % transmission). No obvious impact on humification was shown in the ecological experiment, however these results are complicated by probable intra-plot variation and the limitations of the experiment. There is therefore a great deal of
uncertainty regarding the impacts of volcanic acid deposition on peatland acidity and the ways in which any affects might be shown in the palaeoecological record. Any impact on peatland acidity is only likely to be associated with heavy acid deposition and would therefore almost certainly be associated with the impacts on plants discussed in the previous paragraph.

Deposition of tephra on the peatland may also supply elements that might be toxic or more probably might be limiting nutrients within the oligotrophic peatland system (Hodder et al. 1991, Hotes et al. 2004). The way in which any impact by this mechanism might be represented in the palaeoecological record is uncertain. Supply of nutrients might encourage plant growth possibly favouring species adapted to more mesotrophic conditions (maybe favouring monocotyledons over Sphagnum). Similarly with testate amoebae an improved nutrient supply might favour those more nutrient demanding species. An input of sulphur in volcanic acid deposition might also enhance the activity of sulphate reducing bacteria decreasing methanogenesis. An increase in microbial decomposition processes could also lead to increased peat humification and UOM abundance.

There is also the potential that tephra may have an impact through its physical properties. Tephra might cause abrasion to plant surfaces and blocking of stomata, a tephra layer on the peat surface might inhibit gas exchange. These impacts might be represented in the macrofossil record as a shift away from bryophytes, which can be expected to be most sensitive due to the lack of a cuticle. Any impacts on the testate amoebae or humification records is uncertain. No detectable impacts on any proxies were noted in the plots with tephra alone applied in the ecological experiment potentially counting against this theory.

Perhaps the most likely mechanisms by which detectable impacts in the palaeoecological record might be produced would be a direct impact on plants with consequent impacts on the wider ecosystem and impacts through the chemical input of tephra. Changes to peatland acidity are also possible although this is uncertain. The possible modes of impact and their affects on the palaeoecological record are summarised in Table 7.3.1. Changes in the palaeoecological records across the tephra layers can be assessed against this table to help determine the modes of impact. As can be seen there is
a degree of uncertainty over the response to many of the possible impacts and many of the possible processes could have antagonistic affects on the palaeoecological record.
<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Impact on Pharmacological Effect</th>
<th>Immediate</th>
<th>Testable</th>
<th>Measurable</th>
<th>Pharmacological Record</th>
<th>Likelihood</th>
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<td>Possibly increased</td>
<td>Uncertain</td>
<td>Decreased, increase in species</td>
<td>transition</td>
<td></td>
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<tr>
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<td>Possibly increased</td>
<td>Uncertain</td>
<td>Decreased, increase in species</td>
<td>transition</td>
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<tr>
<td>Decreased species' niche</td>
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<td>Possibly increased</td>
<td>Uncertain</td>
<td>Decreased, increase in species</td>
<td>transition</td>
<td></td>
</tr>
<tr>
<td>Increased similarity to acrobiphilic</td>
<td>Possibly increased</td>
<td>Possibly increased</td>
<td>Uncertain</td>
<td>Decreased, increase in species</td>
<td>transition</td>
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<tr>
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<td>Uncertain</td>
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<td>transition</td>
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<tr>
<td>Decreased similarity to non-acrobiphilic</td>
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<td>Possibly increased</td>
<td>Uncertain</td>
<td>Decreased, increase in species</td>
<td>transition</td>
<td></td>
</tr>
</tbody>
</table>

Discussion:

Table 7.3. Possible mechanisms of volcanic impact on ecosystems with an assessment of how they might be portrayed in the pharmacological record and the likelihood of these impacts occurring and being detectable based upon the available literature.
7.4 VOLCANIC IMPACTS ON INDIVIDUAL PROXIES

Having reviewed the mechanisms by which volcanoes might affect peatlands, the palaeoecological evidence can be assessed systematically to determine the extent to which it supports each of these mechanisms. The palaeoecological evidence for changes coincident with each tephra layer is summarised in Table 7.4.1.

7.4.1 Testate amoebae

Impacts on testate amoebae are variable. Although some profiles show extremely convincing evidence for significant change coincident with tephra deposition, other profiles show little or no evidence. The only profiles in which the changes were assessed to be statistically significant were ST 12 and LNA 100. In ST 12 the most significant changes are a significant drop in abundance of *Amphitrema flavum* and a loss of *Hyalosphenia papilio* at the tephra peak. In LNA 100 *Amphitrema flavum* abundance declines below the tephra layer but is actually increasing at the time of the tephra peak. The most distinct changes at this site are a loss of *Difflugia pulex* and increased *Amphitrema stenostoma* and *Amphitrema wrightianum*. Zonation analysis and qualitative data inspection also suggest significant changes in the ECR 162 and ECR 100 profiles. In ECR 100 this change is characterised by a loss of *A. flavum* and *H. papilio* and increases in *Difflugia tuberculata* and *Phryganella acropodia*. In ECR 162 the data show a loss of *A. flavum* and increases in *Bullinularia indica* and *Heleopera sphagni*. Results from these profiles show little similarity in response. In ST 12 and ECR 100 there is a distinct loss of *H. papilio*, however in LNA 100 there is an apparent increase. In three of the profiles there is a loss of *A. flavum*, however in LNA 100 percentages are actually increasing by the time of the tephra peak. ECR 162 shows a large increase in *B. indica*, however in LNA 100 there is a possible decrease in this species. Overall none of the major species show a consistent response to tephra deposition in these four profiles. Table 7.4.2 shows changes in several major species across the tephra layer in all the analysed peat profiles. Changes are qualitatively assessed as an increase, decrease, no change or that the species
<table>
<thead>
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<th>Test</th>
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<tr>
<td></td>
<td></td>
<td>MTR 190</td>
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<td></td>
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<td></td>
<td></td>
<td>ECR 32</td>
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</table>

**Discussion**

Table 7.4.1 Summary of threats impacts on the greenhouse effect.
is not sufficiently abundant to make a judgment. There is little consistency in these changes, for instance *A. flavum* is judged to increase in abundance across three tephras and decrease in abundance across three others. On the strength of this table, the most consistent impacts are on *A. catinus*, which increases abundance across all four tephras in which a distinct change is noted. Equally, *P. acropodia* also increases across all tephras where a change is noted, however some of these changes are indistinct.

There is no convincing evidence that certain testate amoebae species are particularly affected by volcanic impacts. Although several species show major changes coincident with tephra deposition these are generally not replicated between profiles. This suggests that changes are not due to direct toxicity of volcanic products on some species. Instead it seems more probable that changes are due to a volcanic forced environmental change. This would affect different profiles differently depending on their pre-existing state.

To investigate the possible causes of this environmental change the species data has been quantitatively interpreted using transfer functions for two environmental variables: DWT and pH. Initially considering the four profiles in which impacts seem most distinct (LNA 100, ST 12, ECR 100 and ECR 162) there is little consistency in response. In terms of TI-DWT, the tephra peak coincides with minor peaks in ECR 162 and ST 12, a minor trough in ECR 100 and a declining trend in LNA 100. In terms of TI-pH the tephra peak coincides with a peak in LNA 100, a minor peak in ECR 100, an increasing trend in ST 12 and little change or a minor trough in ECR 162. These results demonstrate little consistency in response. Many of these apparent changes do not exceed the bootstrapped error estimates for the values. One of the few consistent changes to exceed the error estimates is a general increase in TI-pH in ST 12, however this trend starts from the base of the profile and cannot be attributed to a volcanic impact.

If the other data sets are also considered there is similar inconsistency. Considering TI-DWT initially, if the tephra peak sample is compared to those on either side four data sets show peaks of varying size (MP 27, ST 24, ST 12, and ECR 162), three show troughs (MP 10, ECR 100, ST 36), two show declining trends (LNA 100, MP 39), one shows an increasing trend (LNA 39), and one shows little change (CHP 33). Considering TI-pH, four data sets show peaks (ECR 100, LNA 39, MP 10, MP 27), two
show minor troughs (ECR 162, ST 24), four show declining trends (MP 39, ST 36, LNA 39, CHP 33) and one shows an increasing trend (ST 12). Although this is a very narrow way of interpreting any change there is no clear evidence from either the TI-DWT or TI-pH results for any consistency in response.

Overall the testate amoebae results show evidence for a volcanic impact in some profiles but not in others. The testate amoebae response to a volcanic impact appears to vary between tephras and does not produce a characteristic response in terms of species changes or TI-DWT and TI-pH. The lack of a consistent increase or decrease in inferred pH or DWT coincident with the tephra layer suggests that changes are not due to these variables.

**Table 7.4.2** Changes in selected testate amoebae species across tephra layers. ‘+’ denotes an increase in abundance, ‘−’ denotes a decrease in abundance, ‘O’ denotes no change in abundance and ‘P’ shows that the species is absent or only present in small quantities. ~ indicates that there is some uncertainty involved in the judgment.

<table>
<thead>
<tr>
<th></th>
<th>A. flavum</th>
<th>A. stenostoma</th>
<th>A. catinus</th>
<th>Difflugia spp.</th>
<th>H. papilio</th>
<th>P. acropodia</th>
<th>T. arcula</th>
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<tr>
<td>CHP 33</td>
<td>+</td>
<td>/</td>
<td>O</td>
<td>/</td>
<td>O</td>
<td>~+</td>
<td>O</td>
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<tr>
<td>ECR 100</td>
<td>-</td>
<td>+</td>
<td>/</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>~</td>
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<tr>
<td>ECR 162</td>
<td>−−</td>
<td>O</td>
<td>/</td>
<td>/</td>
<td>O</td>
<td>~+</td>
<td>/</td>
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<tr>
<td>LNA 39*</td>
<td>+</td>
<td>O</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>LNA 100</td>
<td>+</td>
<td>+</td>
<td>/</td>
<td>−</td>
<td>+</td>
<td>/</td>
<td>−</td>
</tr>
<tr>
<td>ST 12*</td>
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<td>/</td>
<td>/</td>
<td>/</td>
<td>−</td>
<td>~+</td>
<td>~+</td>
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<tr>
<td>ST 24</td>
<td>−+</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>O</td>
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<td>O</td>
</tr>
<tr>
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<td>/</td>
<td>−−</td>
<td>+</td>
<td>/</td>
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<tr>
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<td>/</td>
<td>+</td>
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</tr>
<tr>
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<td>/</td>
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<td>+</td>
<td>/</td>
<td>/</td>
<td>+</td>
<td>/</td>
</tr>
<tr>
<td>MP 39</td>
<td>/</td>
<td>/</td>
<td>+</td>
<td>/</td>
<td>O</td>
<td>−</td>
<td></td>
</tr>
</tbody>
</table>

* For the MP 27 tephra it was not possible to count testate amoebae for the sample containing the tephra peak. * For the LNA 39 and ST 24 tephras there is some uncertainty over the precise location of the tephra peak.

**Problems with the methodology**

Identifying and characterising change in testate amoebae communities is complicated due to a number of factors. The quantitative inference of testate amoebae data using transfer functions is impaired by the lack of some species from the training set. Key species, particularly *Difflugia* spp. are absent from the training set and therefore the TI-DWT and TI-pH reconstructions probably have large associated errors where these
discussion

Species are abundant. This is particularly problematic across tephra layers in the Moose Pass site where \textit{D. cf pristis} and \textit{D. pulex} were frequently encountered. This may limit the ability to identify volcanic induced change in these profiles.

Testate amoebae concentrations were not calculated in this study and all the testate amoebae diagrams and analyses were based on percentages. This means that species results are inter-dependent. It is therefore possible that changes in one species will produce percentage changes in others without any real abundance change. This may make it appear that impacts related to tephra deposition are more widespread than is really the case and complicate identification of any species-dependent affects. This provides a limitation to both quantitative and qualitative data interpretation.

The statistical analyses also have some limitations. The zonation analyses can only provide circumstantial evidence for a volcanic impact. The methods used also have specific problems as discussed previously. By using multiple methods based on differing principles the specific problems associated with individual methods should be largely eliminated. The RDA methodology provides a stricter test of the volcanic impact hypothesis, however this method also has some associated problems. The method relies on the assumption that the volcanic impact variable is a reasonable approximation of how a real volcanic impact would be represented in the palaeoecological record. This model shows a large impact coincident with tephra deposition, this impact declining with time (i.e. depth) and with differences in the testate amoebae community above and below the tephra. It is possible that this is incorrect if the response is lagged behind tephra deposition or the response starts below the tephra peak, however this is not considered likely.

7.4.2 Humification

The second palaeoecological method used to investigate volcanic impacts was peat humification analysis. The humification plots provide evidence that humification analyses are unreliable where there is an abundance of inorganic material. In the plots across large tephra layers, corrected transmission values appear to be primarily controlled by the loss-on-ignition (LOI) values rather than the raw transmission data. Where the raw
Discussion

Humification data show an increased transmission across the tephra layer (due to the relative reduction in the quantity of organic material in the sample) the corrected data show a proportional decrease. These humification changes show transmission values decreased by up over 20% in some sites; these are highly significant changes and would be easily detectable in the visible stratigraphy of these sites. However no such large, visible change can be seen in these samples, indicating that this pattern is an artefact of the methodology used rather than a genuine result.

Measured transmission values were corrected for LOI using the formula

$$H_c = \frac{H_r}{1/L}$$

where $H_c$ is the corrected transmission value, $H_r$ is the raw transmission value and $L$ is the loss-on-ignition value expressed as a proportion. This formula was derived from experiments conducted by Blackford & Chambers (1993) involving the successive addition of mineral material to peat samples. The formula is routinely applied in peat humification studies and usually makes only very minor differences to the corrected values. The large disparity between measured and corrected transmission values suggests some aspect of humification measurement or correction is not working correctly where LOI values are low.

A possible reason for this is that some tephra particles are small enough to pass through the filter. The Whatman Qualitative 1 filter paper commonly used in humification analysis (Blackford & Chambers 1993) retains particles larger than around 11 μm diameter (Whatman plc 2005; www.whatman.com). Particle size analysis shows that the visible tephra layers contain a significant proportion of particles smaller than this size. This would therefore allow particles through the filter to reduce the measured transmission of the solution (Aaby & Tauber 1975) and when corrected for LOI would produce an unrealistically low transmission result. The particles used by Blackford & Chambers (1993) are described as a clay which would indicate particles of less than 2 μm diameter. It is therefore possible that these particles could have passed through the filter however this may be complicated due to the possible adsorption of humic acids onto clay particles. Due to the differences in particle properties between the clay used in the experiment of Blackford & Chambers (1993) and tephras, two experiments were carried out here.
In one experiment a single sample of tephra-free peat was deliberately contaminated with tephra and humification measured. Peat from the Moss of Achnacree site was dried and ground with 0.2g used in each sample. Volumes of Icelandic Öraefajökull tephra (sieved at 150μm) of between 0.002 and 0.075g were added to each sample. Results are shown in Fig. 7.4.1. If tephra penetrates the filter then transmission values should be decreased with increasing tephra added. The results show a great deal of variability but little overall trend, indeed at the highest tephra additions transmission values are highest. There is therefore no evidence that tephra penetrates the filter papers. Transmission values vary between 43 and 49%; if this is solely due to experimental error then this indicates a worryingly high level of imprecision, however heterogeneity in the peat composition may also have an effect.

In a second experiment the humification across a large tephra layer was measured with both the standard and a finer filtration. The ST 36 tephra layer was used in this experiment. Samples were taken at 1cm resolution, 0.1g of dried peat was used in the analyses. Double quantities (100ml) of NaOH were used and so values are not directly comparable with those measured previously. Samples were filtered using the standard method (Whatman 1 filter paper), using a finer filter paper that retains particles greater than 8μm diameter (Whatman 40) and using centrifugation (15 minutes at 4000RPM). The pattern of transmission with the standard method shows the same trends as measured previously. With centrifugation values are increased by 1-2%, particularly towards the centre of the sequence (Fig.7.4.2). With the finer filter paper values are elevated by up to 5% although this is variable over the sequence. The elevated values in the centrifuged and finer filtered samples strongly suggest that tephra particles are penetrating the filter paper used in the standard method. When the transmission values with the finer filter paper are corrected for LOI the large drop in corrected values present with the normal filter is eliminated (Fig.7.4.3). The fine filtration makes significantly more difference to the values than centrifugation. These results therefore demonstrate that measured humification values can be modified by inclusion of inorganic material. The difference between results with the two filter papers suggests that transmission values using the standard method may be primarily affected by tephra particles in the range 8-11μm. The difference in results between the two experiments may be because the Icelandic tephra
Fig. 7.4.1 Effect of tephra additions (g) on measured humification (% transmission)
Fig. 7.4.2 Humification across tephra layer with varying standards of filtration

Fig. 7.4.3 Humification across tephra layer with higher standard of filtration, corrected for LOI
used in the initial experiment was coarser and did not pass through the filter. This indicates that in the Moss of Achnacree experiment the tephra additions are unlikely to have affected the measured humification.

These results show that humification measurement cannot be considered a reliable proxy record across larger tephra layers. However this does not necessarily mean that humification is also unreliable across micro-tephra layers. The tephra layers in southeast Alaska are much smaller and correction for LOI makes very little difference to the values. However in common with the humification profiles across the large tephra layers, most of the profiles across the micro-tephra layers also show reduced transmission values coincident with the tephra peaks. Although reduced transmission values are a conceivable impact of volcanic activity, they are also consistent with an affect of tephra penetrating the filter paper. Although tephra shards are less abundant in these micro-tephra layers, the particle size is smaller and it is probable that a greater proportion of particles pass through the filter paper. Insufficient material remained to test the affect that finer filtration might make to measured transmission values. Although it has not been conclusively demonstrated that depressed transmission values coincident with micro-tephra peaks are due to the effect of tephra particles, caution demands that these changes cannot be considered a record of volcanic impact.

Humification has been measured across tephra layers in several other studies (e.g. Caseldine et al. 1998, Langdon & Barber 2004, Ellershaw 2004). These studies have also used Whatman 1 filter paper. The results presented here suggest a strong likelihood that reduced transmission values noted coincident with some tephra peaks are due to particles penetrating the filter paper and not to a real palaeoecological change. Some of these results must therefore be treated with considerable caution and future humification studies across tephra layers, and in other peats with significant mineral components, should use a higher standard of filtration.

The primary humification change noted coincident with tephra layers in this study is a reduced transmission value at the time of the tephra peak. Although this change must be attributed to tephra particles penetrating the filter, other changes do occur in other profiles. In several of the profiles from southeast Alaska (MTR 32, LNA 39, ECR 100) there are large transmission increases after the tephra peak, some of these changes are
substantial in terms of the full-core record. These changes are not consistent with the affect of tephra particles so it is possible that they do represent a volcanic impact. However these changes are only present in a minority of plots and could be unrelated to volcanic activity. Overall the usefulness of humification results is severely limited by the methodological problems. While it is possible that some humification changes are due to a volcanic impact there is considerable uncertainty in this.

7.4.3 Macrofossils

The final palaeoecological method used is macrofossil analysis. There is reasonable evidence for volcanic impacts upon the macrofossil record in several of the sites. The changes fall into two general patterns. In four of the profiles there is some indication of an increase in Sphagnum percentage coincident with the tephra peak. In two of these, LNA 39 and MTR 146, the change is a sustained increase in Sphagnum through the upper part of the profile with no return to pre-tephra conditions. In two further profiles, MP 27 and ST 68, the change is more short-lived. In ST 68 the data shows a pronounced peak in Sphagnum immediately after tephra deposition, this peak is the only change within the sequence and lasts for 2cm. In MP 27 the tephra peak coincides with a short-lived phase of Sphagnum domination, this phase starts near to the start of the decline in LOI values and ends shortly after the LOI trough. Given the decline in Sphagnum immediately after the tephra peak, the impact of tephra deposition in this site could also be interpreted to be an increase in UOM.

In a further five profiles there is evidence for a peak in UOM coincident with the tephra layer. In LNA 465 the change is comparatively minor and may not exceed the errors inherent in the method. In ECR 162 and ECR 32 the change is more distinct and the peak coincident with the tephra layer is either the highest value (ECR 162) or almost the highest value (ECR 32) of the profile. In ST 12, UOM is a comparatively minor constituent however much the highest value is a peak coincident with the tephra layer. In MTR 190 a peak of UOM coincident with the tephra has a percentage value more than twice that of any other sample in the profile. Coincident with these UOM peaks are peaks of Ericales in ECR 32 and LNA 465 and a highly distinctive peak of Monocots in ST 12.
Overall the evidence for change in the macrofossils across these tephras is more convincing for an increase in UOM than for an increase in Sphagnum. Two of the four profiles in which a Sphagnum increase was noticed show a pronounced and continued increase. A volcanic impact would be expected to be relatively short lived, which may count against these changes being volcano related. In the two further profiles where Sphagnum increases were noted, the peak in ST 68 occurs slightly above the tephra and so could be unrelated, the results in MP 27 could show a Sphagnum phase but could also be interpreted as a post tephra deposition increase in UOM. While it is possible that both increases in UOM and Sphagnum could be related to tephra deposition the evidence for an increase in UOM is more convincing. Several profiles show peaks in UOM which are exactly coincident with tephra deposition and many of which are of high magnitude. Overall the evidence for impacts on the macrofossil record is quite good. While some changes are subtle, others are distinct and of large magnitude.

7.4.4 Consistency between proxies

As discussed in the previous sections both macrofossils and testate amoebae (and also maybe humification) show evidence for changes coincident with tephra layers in some sites. However apparent impacts detected by one proxy-record are not always replicated by the others. Testate amoebae analysis is the most quantitative method used here. Results suggest that impacts are most distinct for profiles ST 12, LNA 100 and to a lesser extent ECR 100 and ECR 162. Macrofossil results show a distinct change across the ST 12 tephra with a peak in monocotyledons and UOM. Macrofossil data across ECR 162 also shows a peak in UOM at the time of the tephra peak. No distinct macrofossil change is noted in LNA 100, in ECR 100 a major macrofossil change is offset from the tephra peak by 2cm. Humification results show distinct increases in transmission values above tephras ECR 100 and to a lesser extent LNA 100.

The macrofossil results show the best evidence for changes coincident with tephra deposition in profiles ECR 32, MTR 190, ECR 162, ST 12, ST 68 and MP 27. Two of these are profiles in which testate amoebae impacts were also noted (ECR 162 and ST 12) while in a further three no testate amoebae could be counted (ECR 32, MTR 190 and
ST 68). In profile MP 27 there is only limited evidence for testate amoebae change coincident with the tephra peak. These results therefore demonstrate that in many cases impacts shown with one proxy-record are not shown by others.
7.5 NATURE AND CAUSES OF VOLCANICALLY INDUCED CHANGES

7.5.1 Is there evidence for a volcanic impact?

Overall the palaeoecological results suggest some evidence for changes coincident with the tephra layers but these changes are not present in all profiles. In the testate amoebae data two data-sets are assessed as statistically significant using RDA and the volcanic impact model. A further two data-sets show evidence for change coincident with the tephra peak when assessed qualitatively and using zonation analyses. In the macrofossil results a qualitative assessment of the data suggests large changes coincident with at least four, and perhaps six or more, of the tephras. Humification results are unreliable but in some profiles there are changes that are not consistent with simply the affect of tephra particles penetrating the filter paper.

While it is possible that some of these changes may be coincidental the proportion of sites in which a distinct change occurs coincident with the tephra layer is greater than would be expected by chance. Evidence is most convincing for the two profiles in which the volcanic impact model described a significant proportion of the variance in the testate amoebae data. These results show that not only is change occurring but that this change is consistent with what would be expected as a response to a volcanic impact.

Overall, the results therefore demonstrate that in some profiles and with some proxies there are changes coincident with tephra deposition and that in some of the profiles these changes are statistically consistent with a volcanic impact. However, these changes are not found across all tephras and where they are found with one proxy-record they are not always found by other proxy-records. The possible causes of these changes and the reasons for the lack of a response in all the profiles are discussed in the subsequent sections.

7.5.2 Complicating factors

Attributing palaeoecological change to volcanic action is complex due to several factors. One of the most significant of these is the complexity of some tephra
concentration profiles. In two of the sites (LNA 39 and ST 24) the tephra profile was multimodal and it was difficult to determine where the isochrone was located. This makes it difficult to accurately identify any relationship between the tephra peak and palaeoecological change. In another site (MP 27) the tephra layer itself meant that it was not possible to count testate amoebae from a sample which made it more complicated to identify volcanic induced changes.

A further factor may have been the resolution of the sampling interval. Samples represented between approximately 10 and 60 years. A higher sampling resolution was not possible due to the availability of material and concentration of tests. It is possible that some impacts may have had only a short duration- a few years or less. These impacts would not have been detectable by this methodology. It is therefore entirely feasible that shorter-term impacts did occur in some sites but were not detected here.

The above discussions have assumed that a volcanic impact will be represented as starting coincident with or directly above the tephra layer. However, there are several reasons why this may not be the case. Firstly, as has been discussed previously this may be complicated by post-depositional movement of tephra down through the peat. The taphonomy experiment suggests that this is likely to be limited, however with the restricted nature of the experiment and the differences in peatland structure, vegetation and hydrology between the experimental site and the Alaskan sites, this cannot be totally discounted. Secondly, it is possible that there may be some inertia in the system and a response to volcanic impacts may be slightly lagged behind the event. In general, peatland palaeoecological studies do not have the stratigraphic precision to investigate whether a change in the proxy record is slightly lagged behind the actual climatic change (which may be dated by other methods). Palaeoecological studies of recent peats have however demonstrated reasonable agreement between proxy-records and measured water tables or climate suggesting that this is unlikely (Charman et al. 2004, Schoning et al. 2005). A final complicating factor is the possibility for a change in the palaeoecological record to start below the tephra layer; this is most relevant to testate amoebae analysis. In peatlands it is common for testate amoebae to be living several cm below the peat surface (Heal 1962, Corbett 1973). Testate amoebae have relatively fast reproduction, and respond rapidly to environmental changes (Lousier 1974, Clarke 2003). Therefore if there
is a volcanic induced species composition change and assuming tephra stays at the peat surface it is conceivable that this change might start below the tephra layer. Humification might also change below the tephra layer due to changes in peat accumulation rate or decomposition processes in sub-surface peat. While these mechanisms seem feasible there is no evidence that they are occurring. In the sites in which distinct impacts are noted these take place directly coincident with the tephra peak. In other profiles there are rarely any major changes either shortly below or shortly above the tephra peak. Those changes associated with the tephra layers assessed as statistically significant are the most distinct changes noted at any point in any of the profiles. It therefore seems probable that volcanic induced impacts recorded in the palaeoecological record will occur directly coincident with the tephra peak.

7.5.3 Characterising the palaeoecological response

The palaeoecological response to a volcanic impact appears to be variable. The testate amoebae data show distinct changes in some profiles but little consistency in species response to tephra deposition. Species which undergo declines coincident with tephra deposition in some sites undergo increases in other sites. There is a similar lack of consistency when the results are interpreted by transfer functions. While distinct changes in TI-pH or TI-DWT are present across some tephras, across others there is no change or an opposite change.

The most distinct change in macrofossil composition is a peak in UOM present in several profiles. Some profiles also show increase in monocotyledons and Ericales associated with these peaks. A few profiles show increases in *Sphagnum* but this is considered less likely to be related to volcanic activity. The humification results are unreliable but there is evidence for a post-tephra increase in transmission values in some plots.

The duration of these apparent impacts is difficult to judge due to difficulties of determining the start and end of an impact and the limited dating of the profiles. Impacts on the macrofossil profiles seem relatively short-lived lasting around 1cm. Depending on the accumulation rate of the individual site this suggests impacts lasting between
approximately 10 and 50 years. In the testate amoebae data looking at the major species changes suggests that the testate amoebae communities have largely recovered to their pre-tephra state by the top of the profiles, with the possible exception of LNA 100. Based on the age-depth models for these sites impacts would seem to last between approximately 100 and 200 years.

7.5.4 Causes of the impacts

The introductory chapter has highlighted a variety of mechanisms by which volcanoes might affect peatlands. The results can be compared against these theoretical models to identify the possible mechanism of impact. Volcanoes might cause a change in peatland hydrology. This may be possible through a volcanic impact on climate (volcanic induced cooling) producing increasing mire surface wetness. Tephra deposition could also directly affect mire hydrology perhaps causing surface ponding. Plant kills due to the effect of volcanic products could reduce transpiration leading to increased surface wetness. The palaeoecological evidence does not support any of these hypotheses. The testate amoebae species data do not show consistent post-tephra increases in hydrophilic species and the transfer function inferred results do not show consistent decreases in TI-DWT. The macrofossil data also do not show relative shifts towards more hydrophilic components. These results also provide no support for the contrary affect, a reduced mire surface wetness. Although the macrofossil evidence provides some evidence for an increase in drier indicating components, this is not supported by either the testate amoebae species data or TI-DWT. It therefore seems clear that the palaeoecological changes are not due to a hydrological change and the indirect (climatic) volcanic impact hypothesis can be rejected.

A further possible impact is a volcanic induced change to peatland acidity. Either a decrease or an increase is conceivable. There is little evidence to support this hypothesis. The testate amoebae data do not show a consistent response in terms of acidophilic species or in TI-pH. The impact on the macrofossil data cannot be convincingly attributed to either a positive or negative pH change.
It is possible that the direct physical impact of tephra deposition might affect peatland functioning. Tephra layers could cause abrasion to plant surfaces, blocking of stomata and limitations to gas exchange. It is uncertain how these impacts would be represented in the palaeoecological record, however any affect seems unlikely. The ecological experiment found no evidence for impacts in the plots with tephra alone applied. In the palaeoecological studies impacts were present in both the proximal and distal sites, indeed impacts were marginally more frequent in the distal sites. If the impacts were due to the physical impact of tephra it seems likely that they would be more pronounced with thicker tephra layers. Physical impacts of the micro-tephra layers in southeast Alaska seem improbable given the limited extent of these layers. Therefore overall, the physical impacts of tephra seem unlikely to be the cause of the palaeoecological changes.

A further hypothesis for the changes is that they are caused by chemical changes induced by tephra deposition. Impacts may be produced through the contribution of compounds adsorbed to the surface of the tephra shards and tephra leachates. Such an impact might produce impacts on peatland organisms through direct toxicity or by providing limiting nutrients. An impact of this type could produce changes in testate amoebae community but this would not produce a consistent response in terms of TI-DWT or TI-pH. The precise change could depend on the pre-existing nutrient state of the site. To the extent that this mechanism would produce impacts which are difficult to characterise in terms of TI-DWT and TI-pH the observed results support this hypothesis. Chemical changes through tephra deposition might also be associated with direct impacts on plants, which could be consistent with the macrofossil changes observed. The palaeoecological data therefore provide some support for this mechanism.

A final hypothesis is that volcanic acid deposition or volcanic gases could cause impacts on peatland plants. These impacts could be associated with changes in the below-ground environment through physical and chemical changes and changes to food sources, with consequent impacts on microbial communities. Such an impact could produce an impact on testate amoebae without producing a consistent response in terms of TI-DWT or TI-pH, this is consistent with the observed results. The ecological experiment has demonstrated the possible potential for volcanic acids to produce impacts on peatland
plants. Bryophytes may be particularly affected by these impacts and could have reduced abundance in the palaeoecological record. In the ecological experiment widespread plant death was produced and recolonisation took some time. It therefore seems probable that increased UOM could also be a consequence of an acidity impact. In the macrofossil results the most commonly seen affect is an increased proportion of UOM. Decreased Sphagnum abundance is also seen in some sites although it increases in others. The palaeoecological data therefore also provide some support for this mechanism.

Overall, the observed affects are best explained by the final two hypotheses—impacts due to tephra leachates and adsorbed compounds and impacts due to volcanic acid deposition or volcanic gases. Both of these mechanisms potentially explain the observed affects and are feasible. The impacts are difficult to differentiate and may well both have occurred. The ecological experiment has demonstrated the potential impacts of volcanic acids on peatland plants. Given the small size of the micro-tephra layers in southeast Alaska substantial impacts of tephra leachates seem relatively unlikely but impacts due to chemicals adhering to tephra shards are possible. Although volcanic impacts on peatlands through other mechanisms cannot be ruled out the evidence suggests they are not dominant in these sites at least.

### 7.5.5 Causes of differential response

These results show a variable response to tephra deposition. In some sites impacts are quite distinct however in other sites no impacts are evident by these methods. There are several possible factors which could have contributed to this apparent differential response.

One important factor may be the size of an eruption. Larger eruptions will produce more tephra which travels further and which may have more adsorbed acids and other compounds. The results provide some indication that this may be an important factor. Of the four greatest apparent impacts (ECR 162, ECR 100, LNA 100 and ST 12) several tephras are from notably large eruptions. The Aniakchak eruption which formed the ECR 162 tephra, the White River eruption which formed the LNA 100 tephra and quite possibly the eruption of Augustine that formed the ECR 100 tephra are all large
eruptions. However there is no evidence to suggest that the eruption that formed the ST 12 was of particularly large magnitude and impacts of this tephra are significant. Therefore the role of this factor is uncertain.

A second potentially important factor is the size of the tephra layer as represented by the tephra shard concentration or thickness of the visible layer. Thicker tephra layers are likely to have greater impacts on peatlands in terms of tephra leachates and greater physical impacts. Of the tephras associated with greatest impacts there is no clear affect of tephra layer size. The larger visible tephras in south-central Alaska are generally not associated with greater impacts than the cryptotehrs in southeast Alaska, indeed there is more evidence for a reverse affect. It therefore seems unlikely that this factor is key. A further important factor is the distance of the site from the source eruption. At greater distance, tephra may have more adsorbed volatiles (Rose 1977, Oskarsson 1980, Smith et al. 1993). Therefore, distal tephras could be associated with greater impacts than proximal layers regardless of the size of the layer. While some of the greatest impacts are associated with tephras at great distance (e.g. ECR 162) impacts of the proximal ST 12 tephra are also considerable. There is therefore limited evidence to support this theory.

It is also possible that impacts may be dependent on the season of an eruption. Modern studies of distal volcanic impacts have shown that plants are generally less sensitive to eruptions outside the growing season (Zobel & Antos 1997, Hotes et al. 2004). In winter plants will be senescent and high rainfall may serve to rapidly remove volcanic pollutants. Impacts may be particularly dependent on snow cover. Snow will stop volcanic products coming into direct contact with the peat surface. In spring snowmelt, volcanic products contained in the snow will be heavily diluted and may be removed by surface water flow. The sites in this study are snow covered for much of the year; meteorological data show an average of around 5 months annual snow cover at Juneau and Haines and six months at Kenai (Western Regional Climate Center; www.wrcc.dri.edu). It is therefore highly possible that snow cover is a significant cause of differential impacts. This issue is difficult to consider as there is very limited evidence for the season of ancient eruptions. An exception to this is the White River Ash (Eastern Lobe), which is believed to correlate to the LNA 100 layer in this study. West & Donaldson (2002) presented geomorphological evidence for this tephra to have been
produced in late autumn or early winter from the preservation of large tephra clasts in fluvial deposits. If impacts of winter eruptions are minor it would therefore seem probable that impacts at the Point Lena site would be minimal. However, the LNA 100 tephra is actually associated with rather significant impacts. This may count against this theory. However West & Donaldson (2002) hypothesise that the eruption was in the very earliest stages of winter. Their sites are both further north and at higher elevation than Point Lena. It is therefore conceivable that Point Lena could have been unfrozen and snow-free at the time of eruption.

It is also possible that tephra impacts may be related to the nature of the site. Any one or more of site vegetation, hydrology and nutrient status could conceivably affect impacts. However there is no particular evidence that this is a significant factor. The most severe impacts were on the Point Lena and Sterling sites. These peatlands are quite different; Point Lena is an ombrotrophic raised bog while Sterling is a kettle-hole peatland which may receive some groundwater input. Different tephras deposited on the same peatland can have a quite different scale of impacts. Although ST 12 is associated with impacts, two other tephras of similar size in the Sterling site are not. This suggests that the variability of impacts is more likely to be due to some other factor and is not closely related to the nature of the site.

A further important factor may be the atmospheric conditions at the time of eruption. Analogues with anthropogenic air pollutants show the potential for prevailing meteorological conditions to lead to highly localised deposition of acidic pollutants (Davies et al. 1984). It is possible that the interaction of meteorological conditions and topography could have led to localized heavy deposition of volcanic acids at some of these sites. It is therefore conceivable that the impacts of the same eruption at a similar distance could have differed greatly through a region. This hypothesis could provide an explanation for the differential impacts but is difficult to investigate directly.

The previous discussion has suggested that the most likely mechanism of volcanic impact is through volcanic gases, acids or tephra leachates. However impacts are only seen in a minority of plots. The most likely factors determining why some tephras produce impacts and others do not, and determining the scale of these impacts would seem to be the meteorological conditions at the time of eruption and the season of
eruption. To investigate which of these is most important further research using both ecological and palaeoecological techniques will be necessary.

7.5.6 Volcanic impacts on peatlands: wider implications

This study provides good evidence that volcanoes have the potential to affect peatlands. Impacts can be detected in records of past plant communities and past microbial communities. The mechanism of these impacts is not entirely certain but most likely relates to deposition of volcanic acids and other compounds adhering to tephra particles. The scale of impacts is variable between tephras; this may be due to the season of the eruption and the meteorological conditions prevalent at that time. While ecological experimentation can indicate the potential for volcanoes to affect peatlands (demonstrated by Hotes et al. 2004 and the Moss of Achnacree experiment), direct observations or palaeoecological study are required to show that this actually takes place. This study provides the first wide-scale investigation of palaeoecological evidence for volcanic impacts on peatlands, the results have several implications for peatlands and the wider environment.

Perhaps the most significant possible implication of these results is the potential consequences for the volcano-climate system. Sulphate additions to peatlands have been shown to suppress methanogenesis (Gauci et al. 2002). It is possible that deposition of volcanic sulphate on peatlands could suppress methane emissions, potentially reducing the atmospheric concentrations of an important greenhouse gas and reinforcing volcanic induced cooling (Stevenson et al. 2003). This study provides the first direct evidence for the ability of volcanic eruptions to affect peatland microbial communities. This therefore provides considerable circumstantial evidence in support of the possibility of changes to methanogenesis associated with volcanic activity. This process could have serious implications for the volcano-climate system and therefore for global environmental change and human populations.

Peatlands constitute a large resource of biodiversity including many species that are specially adapted to the unique physical environment of peatlands. Volcanic impacts could potentially have significant implications for many rare species. If volcanic impacts
are as severe as implied by the ecological experiment then large impacts on sensitive plant populations could result. Knock-on impacts on insects and vertebrates are also possible which may have implications for populations of these species.

Volcanic impacts may have a significant impact on various aspects of human exploitation of peatlands. Peatlands are extensively used for silviculture; commercially exploited conifer species may be sensitive to volcanic acids (Caput et al. 1978). Blackford et al. (1992) have suggested damage to conifer trees associated with volcanic activity, these results provides tentative support for this possibility. It is therefore possible that volcanic impacts could affect peatland forestry. In the USA, peatlands and artificial wetlands are widely used for cultivation of Cranberries \textit{(Vaccinium macrocarpon)}. This industry was valued at $350 million in 1997 (http://www.uga.edu/fruit/cranberri.htm) and is widespread in Oregon and Washington, regions exposed to volcanic activity with relative frequency. Peatlands are also employed for cultivation of \textit{Sphagnum} (used for horticulture) in some regions of the world including volcanically active areas such as southern Chile (http://www.orchid-sphagnum-moss.com/index.htm). This industry could be severely affected by volcanic impacts on peatlands. Peatlands are widely used for peat cutting with peat used both in horticulture and for burning in both domestic and power generation situations. Any volcanic impacts on peatlands are unlikely to severely affect the utility of peat produced, however the inclusion of tephra in peat makes it less optimal for burning (Dachnowski-Stokes 1941).

This research also has wider implications for peatland palaeoecology. These results demonstrate that it is possible for changes in key proxy-records to be caused by a mechanism independent from climate change. It is possible that these changes could be mistaken for a short-term climatic change. This is a particular risk where tephrochronology is not considered or for eruptions which may produce impacts on peatlands without leaving tephra as evidence (for instance Laki 1783). The results show that tephra cannot be assumed to be an inert marker in a palaeoecological sequence. Tephra layers have been used to correlate changes between different palaeoecological sequences (e.g. Landon & Barber 2004, van den Bogaard et al. 2002). Studies of this nature run the risk of mistaking a tephra-impact effect for a synchronous climatic change.
at the sites. This study highlights methodological problems with humification analysis and may suggest that humification results may be unreliable in mineral-rich peat.

This study has demonstrated the potential applicability of peatland palaeoecology for investigating the impacts of past volcanic eruptions on peatlands. Results indicate that the record may not have sufficient resolution to investigate volcanic impacts on climate and that these impacts may be concealed by the direct impact of volcanic products on peatlands.

**Key Findings**
- Volcanic eruptions can affect peatlands
- Impacts are most likely due to volcanic acids and other adsorbed compounds on tephra shards
- Impacts are highly variable, this may be due to environmental factors
- These results have important wider implications, particularly for the volcano-climate system
7.6 FURTHER WORK

7.6.1 Expanding the current study

There are several ways in which this palaeoecological study could be extended if time and resources allowed. Perhaps the most important of these is an extended radiocarbon dating program. Ideally all of the tephras would be wiggle-match dated. This would increase the probability of attributing all the layers to a source eruption. Perhaps morevaluably this could also allow investigations of peat accumulation rate change coincident with tephra deposition. An improved age-depth model would allow the use of alternative statistical techniques such as rate of change analysis to investigate the testate amoebae results (Barker et al. 2000). The macrofossil results obtained in this study could be extended by using a more rigorous classification system, perhaps using the second stage of the QLC method (Barber et al. 1994). Re-sampling of the sites would allow a larger volume of material to be analysed. This might allow testate amoebae counting and electron microprobe data to be obtained from sites where this was not possible or not conclusive in the existing study. Trace element analyses of tephra layers could help confirm the identification of some of the tephra layers.

Other palaeoecological records could also valuably be investigated if sample volume was not a restriction. Oribatid mites are relatively abundant in some of the sites; these organisms have been used as indicators of environmental change in previous palaeoecological studies (e.g. Solhøy & Solhøy 2000) and might be sensitive to some aspects of volcanic impacts. Particularly valuable might be pollen analysis across the tephra layers. Pollen analysis was initially avoided in this study as it was considered unlikely to respond to short-term climatic cooling. In hindsight pollen analysis may have helped to investigate volcanic impacts on the vegetation of both the peatland and in the wider environment. It might also be interesting to take replicate samples across the same tephra at several points in the same site and to examine the palaeoecological record. This could illustrate any spatial differences in response to tephra deposition, which might be due to differences in vegetation or microtopography.
7.6.2 Recommendations for future research- Volcanic impacts on peatlands

As the previous discussion has suggested the work in this study has provided useful information to help our understanding of volcanic impacts on peatlands but we are still a long way from fully understanding these important processes. To do this a variety of further work would be required.

Perhaps most useful would be direct ecological study of volcanic impacts on peatlands, this has not previously been carried out in any systematic way. In regions such as Alaska and Kamchatka, small to medium scale volcanic events are relatively frequent and peatlands are numerous. It is therefore feasible for peatlands to be identified in a region of recent tephra fall and the ecological consequences monitored over a period of time. It would clearly be preferable to monitor the site before tephra-deposition to obtain base-line data. This would be more difficult however, the well-established monitoring network on some Alaskan volcanoes does allow the potential to predict the likely pattern of tephra fall-out from a forthcoming eruption and choose sites accordingly.

Although a monitoring study after a contemporary eruption is sorely required, studies of this type are unlikely to be able to characterise the full range of possible impacts and would be hampered by logistical difficulties. There is therefore a need for experimental studies. Studies of this nature should consider all volcanic products and should liase with geologists to establish the most likely scenarios for past and future volcanic impacts. Studies should investigate the difference that varying tephra volume, particle size and quantity and composition of adsorbed compounds make to the nature and scale of an impact. A more complete range of variables should be investigated to determine the nature of the impacts, these should include quantitative measurements of plant abundance, measurements of plant growth and plant health (such as C:N ratio, flowering, pollen production), investigations of the microbial communities (microbial respiration, testate amoebae counts, genetic analyses), changes to peat and porewater chemistry (pH, cations), changes to hydrology (DWT measurements) and any changes to gas flux (CO₂, CH₃). Experiments should include thorough replication with several control plots. Plot size should be as large as possible and should encompass a range of microform and vegetation types. Ideally experiments should be carried out on several
sites including fens as well as true bogs. Experiments could usefully be conducted in several regions of the world where volcanoes may impact on peatlands (i.e. the North Pacific, New Zealand, South America, Iceland and NW Europe) to investigate the affect that differing vegetation types and climatic regimes may make to any impacts. Laboratory-based experiments may also be valuable to allow closer control of environmental conditions.

Experiments could also be carried out to investigate other aspects of volcanic impacts on peatlands. Leaching experiments should be carried out on recently erupted tephra to investigate the chemical contributions of tephra in the acidic and anoxic peat environment. Further experiments could be carried out to investigate the taphonomy of tephra in peat. These experiments could include a wider variety of tephra applications and particle sizes applied to a variety of vegetation types on a variety of peatlands. Laboratory experiments could be carried out to investigate in detail the impact of varying hydrological regimes on tephra movement. Studies of tephra taphonomy could be combined with those of pollen and other microfossils to investigate any differences in their movement due to differing structure, size and density. Studies of the micro-structure of palaeo-tephra layers would also be valuable to investigate the relationship between tephra layer morphology and peat micromorphology.

Experimental work is only as good as the scenarios it is based on, there is therefore a need for further palaeoecological studies to investigate exactly how past eruptions affected peatlands. Studies should be carried out in all regions where volcanoes may have affected peatlands and should consider a range of tephra layer sizes from a range of eruption sizes. Future studies should include the biological proxy records used in this study and also other micro-fossils such as chironomids, oribatid mites, diatoms, pollen and spores, where present. Studies should use as high a resolution as possible. Some pollen studies have used mm-scale sampling, such a high resolution is difficult with other microfossils due to a lower concentration but may be possible with larger samples. Statistical frameworks such as that adopted here and in previous studies from lakes (Lotter & Birks 1993, Barker et al. 2000, Eastwood et al. 2002) should be used to assess the results, concentration diagrams could usefully be constructed as well as percentage diagrams. Geochemical analyses of peat across tephra layers could help
investigate any impact of tephra deposition upon peatland geochemistry. Such work may encounter the same problem as Charman et al. (1995) of differentiating peat chemical changes from the chemistry of the tephra itself. Solutions to this might be to analyse peat porewater (as carried out by Hodder et al. 1991) or to use a separation method to remove tephra from the peat matrix. Problems might also be posed by the mobility of many chemicals associated with volcanic impacts. Palaeoecological analyses could be combined with high resolution studies of tephra distribution using X-radiography or microtomography to improve understanding of the linkages between the tephra layer and the palaeoecological record.

Peatland palaeoecological research could be combined with other palaeoecological records to provide a more complete understanding of volcanic impacts. The presence of trees living on and preserved in the peat of many mires allows the interesting potential to compare volcanic impacts on the peatland palaeoecological record with impacts upon the dendro-record. The impact of specific eruptions could be investigated in lake sediments and with terrestrial pollen to determine the relative sensitivity of dryland, wetland and aquatic ecosystems.

7.6.3 Recommendations for future research directions- Peatland palaeoclimatology

Further research is also needed in more general peatland palaeoecology and peatland palaeoclimatology. Perhaps the most urgently needed research is on the linkages between peatland hydrology and climate. Peatland palaeoclimatology relies on the assumptions that the palaeoecological record is related to past mire surface wetness and that past mire surface wetness is related to climate. While the first of these assumptions has received a good deal of attention, the second has received remarkably little. That mire surface wetness (in ombrotrophic mires at least) is directly linked to climate is intuitively sensible but has been addressed in few studies. Specifically the main issue is: which is more important- temperature or rainfall? and, does this vary between sites and regions? This issue has been addressed in two recent studies (Schoning et al. 2005, Charman et al. 2004) but these found differing results. Peatland palaeoclimatology now allows quantitative reconstruction of changing mire surface wetness through transfer function
models. However this knowledge is of limited use if we can't determine (and preferably model) how this relates to climate. Further research is therefore needed along the lines of the studies of Charman et al. (2004) and Schoning et al. (2005), from a wider range of sites. This research would be most valuable on those sites where there is a long record of water table measurement.

Further work is also needed on several of the proxy-records that have been utilised in palaeoecological studies. For testate amoebae analysis several questions are deserving of further research. An expanded program of transfer-function studies would improve our knowledge of testate amoebae ecology and biogeography in peatlands around the world. Studies should include sites in different regions of the world (away from NW Europe and eastern North America) and in a greater range of peatland types with more fen sites and sites that are not Sphagnum-dominated. Future transfer function studies should endeavour to characterise annual variation in water tables as carried out by Woodland et al. (1998). This may eventually make it possible to compile regional training sets similar to those developed in diatom studies (eg. Bennion et al. 1996). Improved methods may also be investigated for deriving transfer function models. The ML method investigated in this study has not been widely tested and may make a valuable contribution.

More study should be devoted to the decomposition of testate amoebae tests in peat, the species that are particularly susceptible and the environmental conditions that encourage this. This could be addressed using a series of long-term laboratory experiments designed to simulate the environmental conditions in differing peatlands. Efforts should be made to adopt a greater degree of taxonomic explicitness in species description. Attempts are currently underway to compile a unified taxonomic key of all testate amoebae species (Edward Mitchell, personal communication) which should go a considerably way to achieving taxonomic uniformity. The lowest degree of taxonomic division should be adopted wherever possible (Bobrov et al. 1999).

For humification analysis the key issue requiring further research is exactly what the standard alkali extraction-colorimetry method measures. Further chemical research is needed into the precise structure of the chemicals extracted and the extent to which these may depend on the species composition of the peat. The luminescence method described
by Caseldine et al. (2000) may prove valuable in increasing the information obtainable by humification analysis. For macrofossil analysis several further developments are possible. Experiments could be carried out to investigate the differential preservation of plant material in the palaeoecological record and the factors that affect this. This could inform more accurate reconstructions of past mire vegetation. Macrofossils have not been analysed using transfer function approaches due to the more complex ecology of plants. Developments in modelling techniques may make this feasible in the future.
CHAPTER 8. CONCLUSIONS

The central research question of this thesis is ‘Can volcanic activity affect the functioning of peatlands, and if so how do these impacts occur?’ Two working hypotheses were proposed: a) that impacts are due to the direct impact of volcanic products falling on the peatland and b) that impacts are due to a volcanic impact on climate, represented as a change in peatland surface wetness.

Results show that there is evidence that volcanic activity can affect peatlands and has done so in the past. The palaeoecological response is not consistent with a volcano-climate effect and so this working hypothesis can be rejected. Results suggest that impacts are due to the direct impact of volcanic products, the most probable mechanism is believed to be through volcanic acids and gases or other chemicals adhering to tephra shards. Impacts on peatlands are highly variable and are not associated with all tephras, this may be due to the season of eruption or the meteorological conditions at the time of eruption. Further work will be necessary to characterise the precise mechanism of impact and the reasons for the differential response. These results have significant implications for the volcano-climate system, for peatland palaeoclimatology and for the conservation and exploitation of peatlands.

The findings from this thesis however expand further than the central research question. The full-core humification study indicates that peatland development in Alaska is controlled by climate and suggest the potential for peatland palaeoecology to be applied here. The testate amoebae ecology study provides the first palaeo-moisture transfer function from western Alaska. Results demonstrate that testate amoebae communities are controlled by surface moisture and pH. This work will allow quantitative palaeoclimatic reconstruction from Alaskan peatlands.

The experiments in Scotland demonstrate that it is conceivable for volcanic acid deposition to have drastic impacts on peatlands in northern Britain. This therefore lends limited support to the suggestion that volcanic activity may have influenced the Holocene vegetation history of Scotland. The taphonomy experiment shows that tephra moves down through the peat column but this is generally of limited extent. The results provide
general support to the use of tephrochronology in peatlands although further work is required.

Tephra results have significant implications for the tephrochronology of Alaska with consequent implications for volcanic impacts in the past and volcanic hazard assessment in the future. Results show the great potential of micro-tephrochronology to extend the distribution of tephra layers in Alaska. Furthermore, results highlight the great size of several eruptions, improve the dating of others and show the presence of previously unrecognised tephras.
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APPENDIX I
MICROWAVE DIGESTION AND THE GEOCHEMICAL STABILITY OF TEPHRA

Preparation methods for recovering tephra shards from peats have usually taken two approaches. Initial studies (Persson 1971, Dugmore 1989) used an acid digestion procedure; this method is effective at removing organic material but is comparatively time-consuming and involves the use of hot, concentrated acids with associated risks. More recent studies have used an ashing method involving combustion of the organic component, followed by cleaning of the residue using dilute acid (Pilcher & Hall 1992). This method is quicker and simpler than acid digestion and is readily combined with measurements of loss-on-ignition to allow rapid location of the largest tephra layers. However, ashing has the great disadvantage that the heating used to combust the organic component is believed to alter the geochemical composition of the tephra. Impacts of heating are visible as sintering of the shard surfaces (van den Bogaard & Schmincke, 2002). It is therefore not appropriate to use ashing for samples which will be subject to electron-microprobe analysis (EPMA) to determine the provenance of the tephra. In practice it has become routine to use ashing methods to locate the tephra layers, followed by acid digestion to prepare the samples for EPMA. The majority of studies also use an additional stage in the process with an initial ashing at coarse resolution (usually 5cm contiguous blocks) followed by finer sub-sampling to locate the peak concentration (as in this thesis and also Pilcher and Hall 1992, Langdon & Barber 2004). As well as being time-consuming, this three-stage process uses a lot of material (typically 3cm³ per 1cm core depth), which may be significant where only small samples are available. There is therefore an incentive for developing improved methods which are both quicker and require less material.

Microwave digestion methods have become well established in fields such as environmental chemistry and have found some applications in palaeoecology (Parr et al. 2004, Jones & Ellis 1998). These methods use microwave energy to heat the samples which are contained within pressure vessels. Microwave digestion methods have several distinct advantages over conventional methods. As higher pressures are used, reaction
time is decreased and lower volumes of reagents are required. As the reaction vessels are fully enclosed there is less risk of contact with hot acids and as the system is fully automated, there is improved standardisation between samples, batches and laboratories. It seems possible that these advantages may be equally applicable to a method for extracting tephra shards from peat. A microwave digestion method could potentially be used to replace a second ashing stage to produce samples which are directly ready for EPMA more rapidly than could be achieved with conventional acid digestion and saving material. Before such a method is used in practise, it needs to be tested to ensure that it does not alter the geochemistry of the tephra. In this study two tephras were prepared using both conventional and microwave accelerated methods and EPMA results compared between the two (this experiment is also described by Payne & Blackford in press b).

Methods

Two tephra samples were used in these experiments. The first is from the base of the large Akhlu mountains tephra layer believed to be from the caldera-forming Aniakchak eruption. The second tephra is from the tephra at 12cm depth in the Sterling site on the Kenai Peninsula, both tephras are discussed earlier in the thesis. Peat samples across each of these tephras were oven dried and then ground to a powder. The powdered peat was divided in two and 0.1g used in each preparation.

The microwave digestion method was implemented on a CEM MARS-X machine. The dried peat (0.1g) was added to 5ml of concentrated nitric acid and 5ml of distilled water in each of the reaction vessels. The machine was programmed as follows: heating to 170°C for 10 minutes with a 10 minute ramp (warm-up) time and a 15 minute cool-down time. Following the cool-down period, the reaction vessels were opened carefully and the sample decanted into a centrifuge tube containing 5ml of distilled water. The reaction vessel was rinsed out with further distilled water and the rinsings added to the sample. The sample was centrifuged for 5 minutes at 3500rpm and the supernatant poured off, this process was repeated again and the remaining residue poured into a vial ready for analysis.
The conventional acid digestion method used was the standard method as described previously based on the methods of Dugmore (1989) and Persson (1971). The complete process for a batch of 14 samples from when the peat is added to the vessels, takes less than two hours for the microwave digestion method compared to around four hours for the conventional method. As the microwave digestion method does not require close supervision once the machine is started, the actual contact time is further reduced.

Tephras were mounted and examined as described previously. The Kenai samples were analyzed at Edinburgh and the Aniakchak samples at Bergen. Following Hunt and Hill (1993) totals of less than 95% were not accepted. For comparability to the conventional acid digestion method, the major-element composition of the tephras was used as the key-criterion for geochemical change (Dugmore et al., 1992). A more sensitive method of assessing any changes might be to look at the liquid residue; this was not carried out in this study (Pollard et al., 2003).

Results

Results of EPMA analysis are shown in Table A1. The two oxides which show the greatest dissimilarity between methods are shown in Fig. A1 for the Kenai tephra and Fig. A2a&b for the Aniakchak tephra. The results for the Kenai tephra show little obvious difference between the two methods. Fig. A1 shows low K2O percentages are slightly more common in the microwave digested preparation and low Al2O3 percentages slightly more common in the standard preparation but this is not a clear distinction. The results for the Aniakchak tephras are less equivocal. Fig. A2a shows a clear separation between the two preparation methods. The microwave-digested shards are characterised by markedly lower Al2O3 percentages. Average percentages of several of the other major oxides (Na2O, MgO, CaO, SiO2) are fractionally higher in the microwave digested sample (Table A1). This may represent a relative increase in their percentage abundance due to the loss of Al2O3. Although the sample size is relatively small, the marked distinction between the two data-sets is sufficient to make coincidence unlikely.

These differences can be assessed quantitatively using similarity coefficients (Borchardt et al., 1972). Following Riehle (1985) oxides with a maximum value of less
Fig. Al Proportions of two oxides (normalized totals) with standard and microwave digestion methods for Kenai tephra.
than 0.4% are excluded from the calculation, which in this experiment excludes MnO from all data-sets. Beget et al. (1992) considered that a SC of ≥0.95 shows exact correlation while a SC of 0.90-0.94 may indicate a different tephra from the same source and a SC < 0.90 indicates no correlation.

Results show SC values of 0.98 for the Aniakchak tephras and 0.97 for the Kenai tephras. These values indicate only a small degree of difference between the two preparation methods and by the standards of Beget et al. (1992) both would be attributed to the same source eruption. The values compare to a SC of 0.98 when the Aniakchak (standard preparation) set is compared to data from the top of the same layer and 0.97 when compared to the same tephra at the Espenburg site. Therefore these similarity coefficients, taken alone, do not provide evidence for changes due to microwave digestion.

A further possible impact of acid digestion methods upon tephra shards is through hydration, reducing the total oxide sum (Dugmore et al., 1992). There is no evidence for this having occurred in these experiments. Average totals for all data-sets are over 97% and although the average total for the microwave digested Kenai sample is slightly lower than the standard method, the reverse is true for the Aniakchak sample.

Discussion

The results for the Aniakchak tephra clearly suggest an impact of the microwave digestion method upon major element composition. There is a clear difference in Al₂O₃ content between the two preparation methods with less aluminium in the microwave digested tephra shards. This difference most likely represents leaching promoted by the higher pressure environment used in the microwave method compared to the standard method.

The lack of such a clear impact on other oxides, particularly the alkali metals (Na,K) is perhaps surprising given their mobility. Although aluminium is listed by Dugmore et al. (1992) among the more likely candidates for possible impacts during acid digestion, it is sodium that is most problematic in studies of tephra geochemistry. Sodium mobility is a persistent challenge during electron microprobe analysis (Hunt and Hill,
Fig. A2a\&b Proportions of four oxides (normalized totals) with standard and microwave digestion methods for Aniakchak tephra.
1993; 2001) and sodium leaching may be significant from some tephras in certain depositional environments (Pollard et al., 2003). In this study no impacts are apparent, Fig. A2b shows reasonably good overlap between the two data-sets and the average Na$_2$O percentage is actually slightly greater for the microwave digested sample.

In contrast to the Aniakchak sample there is no clear impact on the Kenai tephra, indeed the average Al$_2$O$_3$ percentage is slightly higher in the microwave preparation. This lack of impact may be due to the more rhyolitic composition of this tephra or the greater heterogeneity of shard composition, making any impact less distinct.

The inability of similarity coefficients to reveal slight geochemical differences in this study highlights one of their key problems. Similarity coefficients take an averaged approach, which means that subtle but significant differences in one oxide may be concealed by gross similarity in others. Although the results can be informative, they should not be used in isolation.

Conclusions

This experiment provides evidence that the microwave digestion method used here may affect the geochemistry of some tephras. The changes are subtle and probably would not have affected tephra identification in this case. However, although it remains possible that a microwave digestion method may be adequate for some tephras, in some circumstances, it seems probable that the potential advantages do not justify the risk of geochemical change and subsequent misidentification.

There is a persistent problem of tephra stability in both sample preparation and the depositional environment which this study has further highlighted (Hodder, et al. 1991; Pollard, et al. 2003). Volcanic glass is not a stable medium. Although tephra geochemistry is a highly useful tool it is not without problems and consideration should always be paid to possible post-depositional changes which may occur in the field and in the laboratory.
### Table A1: Geophysical data for geophysics prepared using standard and microwave digestion methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Data 1</th>
<th>Data 2</th>
<th>Data 3</th>
<th>Data 4</th>
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<tr>
<td>Standard</td>
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<td>Microwave</td>
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*Note: Further details can be found on page 359.*