.Distal volcanic ash layers in the Lateglacial Interstadial (GI-1): problems of stratigraphic discrimination

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Abstract

The newly-detected Icelandic Penifiler Tephra occurs in the mid-Interstadial sediments of a number of Scottish Lateglacial sequences. It is rhyolitic in composition and possesses a chemistry which is similar to the Borrobol Tephra of early Lateglacial Interstadial age, which also occurs in a number of these same sequences. Such chemical similarity may account for some of the confusion regarding the age and stratigraphic position of Borrobol-like ash layers occurring elsewhere. However, where the Borrobol Tephra has been identified in these sequences it consistently exhibits a diffuse distribution accompanied in some cases by stratigraphic bimodality. A number of sedimentological and taphonomic factors are considered here in order to account for this distribution. One possibility is that these distributions are produced by taphonomic factors. Another possibility is that the Borrobol Tephra may not be the product of a single Icelandic eruption, but of two events closely spaced in time. In at least two of the sequences investigated in this study, basaltic shards were found in association with the Penifiler and Borrobol ash layers, suggesting either a basaltic phase associated with these eruptions, or coincident eruptions from a separate basaltic volcanic centre. Such basaltic populations may strengthen correlations with basaltic ashes recently detected in the NGRIP ice-core. The detection of the new Penifiler Tephra contributes to the regional tephrostratigrapic framework, and provides an additional isochron for assessing the synchroneity of palaeoenvironmental changes during the Interstadial. The true stratigraphic nature and, therefore, age of the Borrobol Tephra, however, is persistently difficult to resolve making its use as an isochron more problematic.

Keywords: Lateglacial Interstadial (GI-1), volcanic ash, tephrocorrelation, Penifiler Tephra, Borrobol Tephra, lake basin taphonomy

1. Introduction

Tephrochronology has much potential as a tool for assessing the rate and synchroneity of palaeoclimatic and palaeoenvironmental change in terrestrial, marine and ice-core sequences from the Last Glacial-Interglacial Transition (Lowe, 2001; Turney et al., 2001). A number of new Icelandic distal fine ash layers (sometimes also referred to as ‘microtephras’ or ‘cryptotephras’, typically <100 μm in size) have been discovered in recent years which significantly contribute to an expanding tephrostratigraphic framework for Europe and the north-west Atlantic region (Davies et al., 2002). Such ash layers provide the critical high-precision correlation necessary for investigation of the Last Glacial-Interglacial Transition, a period characterised by abrupt environmental changes (Björck et al., 1998). A particularly valuable ash in this respect is the Borrobol Tephra (Turney et al., 1997), which was first detected at the site of Borrobol in north-east Scotland. Its estimated age at this site of ca. 14 400 cal yrs BP (Lowe et al., 1999) places it in a position indicated by loss on ignition (LOI) curves to mark the onset of Lateglacial Interstadial (GI-1) warming.

Subsequent studies, however, have revealed ash layers of similar chemistry to occur later in the Interstadial, as demonstrated by a markedly higher stratigraphic position relative to LOI curves, or significantly later radiocarbon ages (Davies et al., 2004; Ranner et al., 2005; Wohlfarth et al., 2006). Such discrepancies in stratigraphic position and age have led to the speculation that there was more than one eruption from the source of the Borrobol Tephra during the Lateglacial Interstadial (Davies et al., 2004). This has recently been confirmed in a number of Scottish sequences in which the Borrobol Tephra had previously been detected (e.g. Turney et al., 1997) and which have subsequently been found to also contain a mid-Interstadial rhyolitic ash of Borrobol affinity, named the Penifiler Tephra (after a hamlet adjacent to Druim Loch, Isle of Skye) (Pyne-O'Donnell, in press).

A further complication concerns the early Interstadial Borrobol Tephra (sensu Turney et al., 1997), which commonly displays a stratigraphically diffuse distribution (Roberts, 1997; Turney, 1998b). This could reflect either a period of prolonged sediment reworking during the early Interstadial, or several eruption events closely spaced in time, with the potential for confusion and error when attempting precise correlation between records. Furthermore, Interstadial ashes with similar chemistries to those discussed here have been reported at two further sites, at Lochan An Druim, northern Scotland (Ranner et al., 2005), and Hässeldala port, southern Sweden (Davies et al., 2003) with the stratigraphic positions of the ashes differing between these two sites. Therefore, the purpose of this paper is to:

- Clarify the stratigraphic complexity of ashes with a Borrobol chemical affinity in Lateglacial Interstadial records in Scotland

- Examine the hypothesis that the Borrobol Tephra (sensu Turney et al., 1997) consists of two peaks representing separate eruption events
- Propose criteria for clarifying the tephrostratigraphic complexity of the Last Glacial-Interglacial Transition
- Compare the new chemical data in this work with that previously published in the literature

The study is based on analysis of a number of small infilled or partially infilled sites in Scotland (Fig. 1), summary details of which are provided in Table 1.

2. Methods

The sediment infill in the Loch Ashik, Druim Loch and Loch an t'Suidhe basins were extensively cored as part of a high-resolution study of the taphonomy of volcanic ash shards in small lake basins (Pyne-O'Donnell, 2004) using a 1 m Russian sampler to extract cores from lake inflow and central basin locations. The sediment sequences at Borrobol, Tynaspirit West and Whitrig Bog were described by Turney et al. (1997) who reported records of the early Interstadial rhyolitic Borrobol Tephra. Multiple cores collected from these sites during the investigations of Turney et al. (1997) and Turney (1998b) have been kept in cold storage at 4º C. A number of these cores were retrieved from storage for the study of Pyne-O'Donnell (in press). With the exception of Whitrig Bog (a 1 m monolith), which is additionally reported in the present study, these were different cores to those examined by Turney et al. (1997) and Turney (1998b).

The ash shard extraction method used is that outlined in Turney (1998a) with the modifications of Blockley et al. (2005). Contiguous 5 cm-long rangefinder sub-

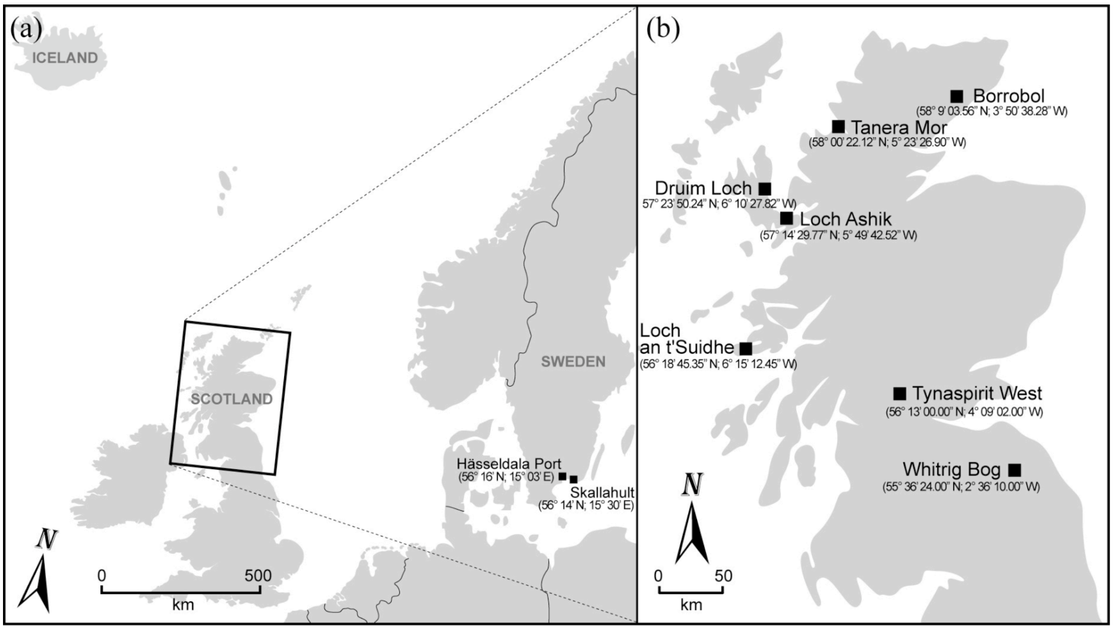
(a)
ICELAND
SCOTLAND
SWEDEN
Hässeldala Port
(56° 16' N; 15° 03' E)
Skallahult
(56° 14' N; 15° 30' E)
N
0
500
km
(b)
Borrobol
(58° 9' 03.56" N; 3° 50' 38.28" W)
Tanera Mor
(58° 00' 22.12" N; 5° 23' 26.90" W)
Druim Loch
57° 23' 50.24" N; 6° 10' 27.82" W)
Loch Ashik
(57° 14' 29.77" N; 5° 49' 42.52" W)
Loch
an t'Suidhe
(56° 18' 45.35" N; 6° 15' 12.45" W)
Tynaspirit West
(56° 13' 00.00" N; 4° 09' 02.00" W)
Whitrig Bog
(55° 36' 24.00" N; 2° 36' 10.00" W)
N
0
50
km

Fig. 1

Table 1

Site name	Location		Sample type	Basin area (km^2)	Drainage area (km^2)	Comments	References
	Latitude	Longitude					
Loch Ashik	57° 14’ 29.77” N	5° 49’ 42.52” W	Russian core	0.02	2.86	Cores from across input and from lake centre with open water	Williams (1977); Walker et al. (1988); Walker and Lowe (1990); Davies (2002); Pyne-O’Donnell (2004); Edwards et al. (2007)
Druim Loch	57° 23’ 50.24” N	6° 10’ 27.82” W	Russian core	0.005	Negligible	Cores from open water. Isolated basin with no inputs or catchment	Walker et al. (1988); Walker and Lowe (1990); Dadswell (2002); Pyne-O’Donnell (2004)
Loch an t’ Suidhe	56° 18’ 45.35” N	6° 15’ 12.45” W	Russian core	0.01	0.25	Cores from infilled margins and open water. Possible palaeo-inputs	Lowe and Walker (1986); Roberts (1999); Davies (2002); Pyne-O’Donnell (2004)
Borrobol	58° 9’ 03.56” N	3° 50’ 38.28” W	Russian core	0.04	49.63	Infilled kettle hole with surface mire	Turney et al. (1997); Turney (1998b)
Tynaspirit West	56° 13’ 00.00” N	4° 09’ 02.00” W	Russian core	0.05	1.88	Infilled kettle hole with surface mire	Turney et al. (1997); Turney (1998b)
Tanera Mor	58° 00’ 22.12” N	5° 23’ 26.90” W	Russian core	Unknown	Unknown	Isolation basin with surface mire	Roberts (1997)
Whitrig Bog	55° 36’ 24.00” N	2° 36’ 10.00” W	Monolith	0.45	10.53	Inter-drumlin hollow with surface mire	Brooks et al. (1997); Mayle et al. (1997); Turney (1998b); Brooks and Birks (2000)

samples were ashed at 550 °C for 2 hrs to remove organics. However, following sieving between 80 and 25 μm, the NaOH treatment stage was replaced by two applications of heavy liquid centrifuge flotation in sodium polytungstate ($Na_6(H_2W_{12}O_{40}).H_2O$) at a density of 2.0 g/cm^3 for 15 min at 2500 rpm. This removes diatoms and other biogenic silica which can obscure microscope identification of glass shards. Rhyolitic ash was then extracted from the mineral-rich sediments by two further applications of sodium polytungstate at a density of 2.5 g/cm^3, which is the optimum density for the flotation of rhyolitic glass. Areas of peak shard concentration within each 5 cm rangefinder interval were identified by optical microscopy using cross-polarised light.

Rangefinder intervals with the highest ash concentrations were then further sub-sampled at 1 cm contiguous intervals (1cm^3 fixed volume) and prepared in the same manner in order to locate the precise stratigraphic depth of maximal ash concentrations. Once located, these depths were sub-sampled and floated again for chemical analysis by electron probe micro-analysis (EPMA) using wavelength-dispersive spectrometry (WDS). Ashing at this stage was avoided, as it is known to alter glass chemistry (Dugmore, 1989). The usual alternative to ashing is to remove the organic fraction by acid digestion. Blockley et al. (2005), however, have demonstrated how prolonged boiling in strong acids, as well as the highly alkaline NaOH stage (Rose et al., 1996) to remove biogenic silica, have the potential to alter the sample yield and chemistry of natural glasses. Accordingly, these steps were omitted and replaced by two centrifuge flotations in sodium polytungstate at 2.0 g/cm^3, which removes organic matter, as well as diatoms, while retaining the denser glass shards.

Chemical analysis of samples by EPMA with WDS was conducted at the Research Laboratory for Archaeology and the History of Art (RLAHA), Oxford, and at the Electron Microscope Unit at Queen's University, Belfast. Results are shown in Table 2 along with details of microprobe analytical settings in the footnotes. Internally assayed Lipari obsidian and NIST 612 glass standards were used to monitor the reliability of data output (Table 3) to ensure consistency of results between both machines and to test for analytical accuracy (Hunt and Hill, 1993). Results for the Oxford machines are included in Table 2.

During light microscope analysis of the mid-Interstadial rhyolitic Penifiler Tephra (floated at 2.5 g/cm^3) detected in a Loch Ashik core, numerous weathered and hydrated brown basaltic glass shards were also observed. The density flotation technique of Turney (1998a) cannot be used to extract basaltic ash shards (density >2.7 g/cm^3) due to the similar density of basaltic glass to other minerals present in Lateglacial sediments, such as quartz (≥2.65 g/cm^3) (Turney and Lowe, 2001). Therefore, a Frantz Magnetic Separator™ was employed following the rhyolitic extraction stage to extract any basaltic shards from the sediments at this site (Froggatt and Gosson, 1982; Mackie et al., 2002).

3. Results

Fig. 2 shows the stratigraphic positions of the Interstadial ashes detected in relation to LOI stratigraphy in each sequence. Multiple cores were analysed in their entirety from Loch Ashik, Druim Loch and Loch an t'Suidhe in the study of Pyne-O'Donnell (2004). However, for brevity only one core has been selected from each sequence for inclusion in Fig. 2 on the basis of the fullest LOI and ash distribution detail. For

Table 2

n	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
[a] Lipari standards (start of run)										
	75.92	0.09	13.05	0.83	0.00	0.11	0.89	3.71	4.55	99.15
	75.62	0.10	12.99	0.88	0.05	0.10	0.82	3.66	4.67	98.89
	75.46	0.10	13.10	0.89	0.08	0.10	0.80	3.65	4.60	98.79
[a] Penifiler Tephra (Loch an t'Suidhe nt7: 641-642 cm)										
1	74.01	0.13	12.49	1.22	0.00	0.05	0.63	3.58	4.17	96.27
2	73.71	0.13	12.65	1.03	0.02	0.04	0.68	3.98	3.92	96.15
3	74.08	0.13	12.37	1.09	0.00	0.04	0.55	3.51	4.08	95.85
4	73.41	0.12	12.47	1.38	0.12	0.06	0.66	3.64	3.90	95.76
5	72.83	0.08	12.05	1.92	0.06	0.16	0.81	3.59	3.93	95.44
6	73.59	0.11	12.24	1.23	0.00	0.01	0.56	3.55	4.12	95.41
7	73.23	0.10	12.30	1.22	0.07	0.05	0.63	3.52	4.11	95.23
8	72.48	0.17	12.68	1.48	0.05	0.09	0.89	3.50	3.86	95.20
9	73.22	0.12	12.37	1.02	0.04	0.01	0.57	3.63	4.14	95.10
10	72.66	0.11	12.16	1.72	0.06	0.12	0.73	3.47	4.04	95.08
11	72.88	0.10	12.31	1.35	0.00	0.06	0.67	3.68	4.04	95.08
12	72.14	0.16	12.69	1.58	0.06	0.12	0.88	3.49	3.91	95.03
13	72.95	0.11	12.28	1.36	0.10	0.07	0.64	3.52	4.00	95.03
14	73.18	0.09	12.20	1.13	0.08	0.03	0.58	3.54	4.17	95.00
Mean	73.17	0.12	12.38	1.34	0.05	0.07	0.68	3.59	4.03	95.40
1□	0.56	0.02	0.20	0.26	0.04	0.04	0.11	0.13	0.11	0.43
[a] Penifiler Tephra (Borrobol: 403-404 cm)										
1	72.64	0.14	12.46	1.51	0.07	0.06	0.74	3.63	3.86	95.11
2	72.59	0.15	12.47	1.45	0.03	0.09	0.80	3.54	3.95	95.06
3	72.62	0.17	12.40	1.46	0.00	0.08	0.78	3.59	3.97	95.06
Mean	72.62	0.15	12.44	1.47	0.03	0.08	0.77	3.59	3.93	95.08
1□	0.03	0.02	0.04	0.03	0.04	0.02	0.03	0.05	0.06	0.03
[a] Lipari standards (end of run)										
	76.13	0.13	13.05	0.90	0.07	0.11	0.87	3.68	4.63	99.58
	76.07	0.13	13.09	0.81	0.06	0.10	0.84	3.74	4.61	99.45
	75.90	0.09	13.02	0.77	0.05	0.12	0.84	3.75	4.57	99.10
[b] Penifiler Tephra (Loch Ashik Isl-W: 933-934 cm)										
1	74.31	0.20	13.76	0.90	-	0.24	1.11	3.79	3.10	97.40
2	72.10	0.15	12.97	1.25	-	0.07	0.69	4.06	3.64	94.92
Mean	73.21	0.18	13.37	1.08		0.16	0.90	3.93	3.37	96.16
1□	1.56	0.04	0.56	0.25		0.12	0.30	0.19	0.38	1.75

[b]Penifiler Tephra (Druim Loch e3: 1000-1001 cm)

1	74.77	0.17	13.13	1.15	-	0.06	0.68	4.20	3.90	98.07
2	74.80	0.14	12.64	1.34	-	0.07	0.71	4.05	3.63	97.39
3	73.98	0.15	13.31	1.15	-	0.05	0.65	3.97	3.69	96.95
4	73.95	0.21	12.60	1.41	-	0.06	0.72	3.92	3.72	96.59
5	73.02	0.16	12.89	1.25	-	0.05	0.66	3.65	3.72	95.40
Mean	74.10	0.17	12.91	1.26		0.06	0.68	3.96	3.73	96.88
1□	0.73	0.03	0.31	0.12		0.01	0.03	0.20	0.10	0.99

[b]Penifiler Tephra basaltic component (Loch Ashik Isl-W: 933-934 cm)

1	46.90	4.28	13.30	14.51	-	4.88	9.67	2.94	0.84	97.31
2	46.83	4.49	13.12	14.76	-	5.18	9.87	3.04	0.81	98.09
3	47.05	4.62	13.21	14.77	-	5.01	9.73	3.11	0.71	98.21
4	47.26	4.53	13.06	15.00	-	4.99	9.70	2.93	0.77	98.25
5	47.20	4.62	13.12	14.81	-	4.99	9.78	3.17	0.74	98.42
6	47.01	4.62	13.14	14.86	-	4.94	10.04	3.10	0.80	98.51
7	47.39	4.75	13.00	14.83	-	5.06	9.70	3.05	0.78	98.56
8	47.04	4.56	12.99	14.94	-	5.06	9.92	3.26	0.80	98.57
9	47.26	4.79	12.97	14.78	-	5.13	9.93	3.26	0.79	98.91
10	47.58	4.63	13.17	14.73	-	5.00	9.85	3.23	0.79	98.97
11	48.01	4.52	13.15	14.93	-	5.00	9.93	2.92	0.80	99.26
12	48.18	4.80	13.13	14.75	-	5.12	10.11	3.07	0.74	99.91
Mean	47.31	4.60	13.11	14.81		5.03	9.85	3.09	0.78	98.58
1□	0.42	0.14	0.10	0.13		0.08	0.14	0.12	0.04	0.65

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[a] EPMA analysis by WDS conducted at The Research Laboratory for Archaeology and the History of Art (RLAHA), Oxford University. Nine elements were analysed using a CAMECA SX50 Scanning Electron Microprobe with accelerating voltage of 15 kV, beam current of 10 nA and a focusing beam size of 10 µm with a diffuse spot.

[b] EPMA analysis by WDS conducted at the Electron Microscope Unit at Queen's University, Belfast. Eight elements (Mn excepted) were analysed using a Jeol 733 Superprobe with accelerating voltage of 15 kV and beam current of 10 nA. In order to reduce migration and underestimation of Na, the beam was slightly defocused to a diameter of ca. 8 µm, with this element being analysed first.

For both machines, oxide abundances (% weight) were calculated by the ZAF correction program of Sweatman and Long (1969), and Lipari obsidian standards (see Table 3) were used in order to test for analytical accuracy (Hunt and Hill, 1993).

Table 3

SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total	
Internal Lipari standard results for analyses:										
75.8	0.1	13.1	0.8	0.1	0.1	0.9	3.8	4.5	99.1	Mean
0.3	0.0	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.4	1□
Expected:										
76.0	0.1	12.7	0.8	0.0	0.1	0.9	3.8	4.2	98.6	Mean
0.5	0.1	0.4	0.1	0.0	0.0	0.0	0.2	0.1	0.4	1□
Lipari for verification:										
73.37	0	12.66	1.1	0	0.28	0.69	3.8	4.8	Min.	
74.67	0.22	12.82	1.66	0.07	0.07	0.77	4.3	5.38	Max.	
Lipari assay reported in Hunt and Hill (1996, 2001):										
73.03	n/a	12.7	1.18	0.03	0.02	0.69	3.73	4.99	Min.	
74.82	n/a	13.03	1.65	0.7	0.08	0.05	4.07	5.48	Max.	

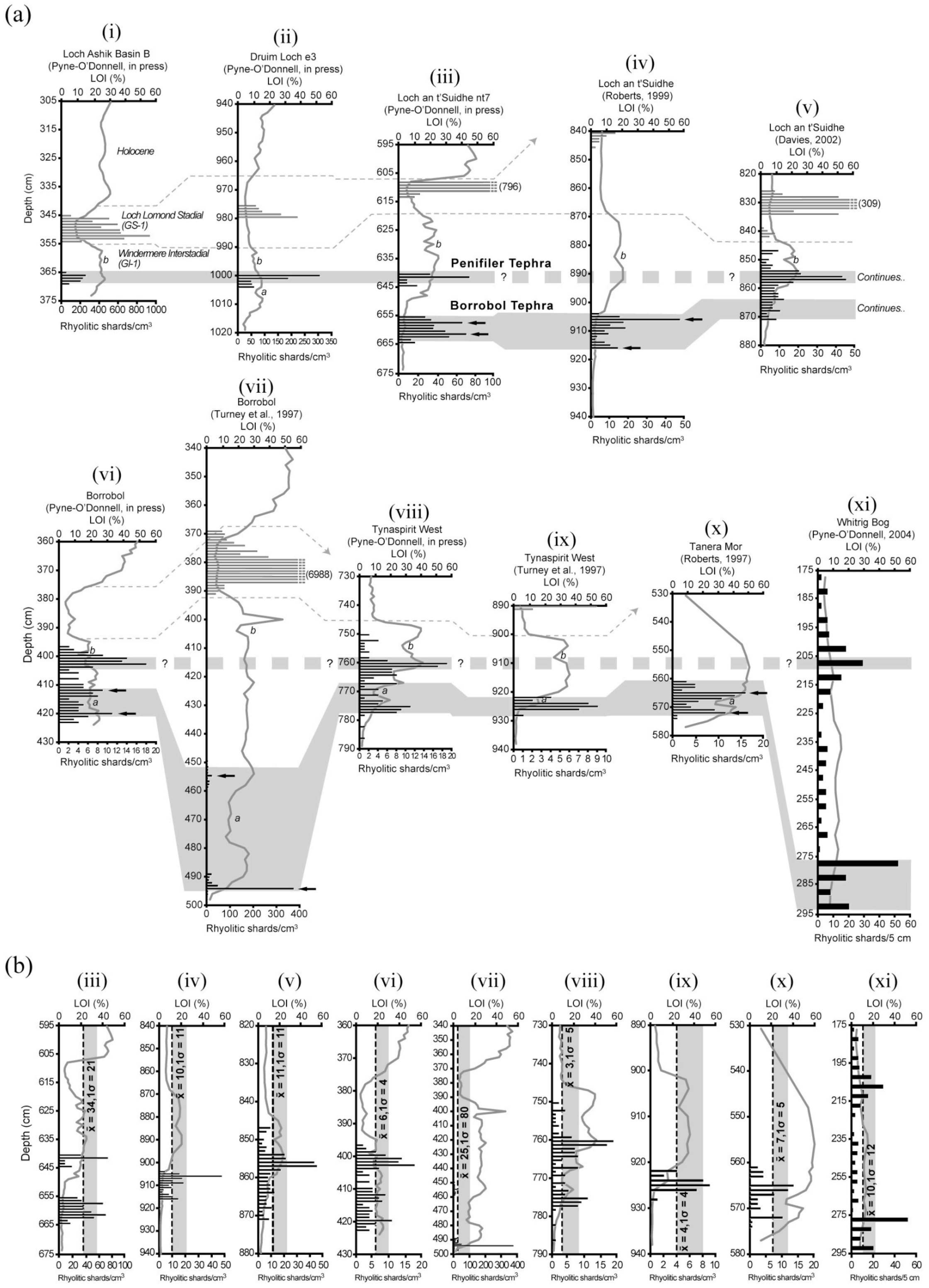
(a)
(i)
Loch Ashik Basin B
(Pyne-O'Donnell, in press)
LOI (%)
Holocene
Loch Lomond Stadial
(GS-1)
Windermere Interstadial
(GI-1)
Rhyolitic shards/cm³
Depth (cm)
(ii)
Druim Loch e3
(Pyne-O'Donnell, in press)
(iii)
Loch an t'Suidhe nt7
(Pyne-O'Donnell, in press)
(796)
Penifiler Tephra
Borrobol Tephra
(iv)
Loch an t'Suidhe
(Roberts, 1999)
(v)
Loch an t'Suidhe
(Davies, 2002)
(309)
Continues..
Continues..
(vi)
Borrobol
(Pyne-O'Donnell, in press)
(vii)
Borrobol
(Turney et al., 1997)
(6988)
(viii)
Tynaspirit West
(Pyne-O'Donnell, in press)
(ix)
Tynaspirit West
(Turney et al., 1997)
(x)
Tanera Mor
(Roberts, 1997)
(xi)
Whitrig Bog
(Pyne-O'Donnell, 2004)
Rhyolitic shards/5 cm
a
b
?
(b)
(iii)
x̄ = 34,1σ = 21
(iv)
x̄ = 10,1σ = 11
(v)
x̄ = 11,1σ = 11
(vi)
x̄ = 6,1σ = 4
(vii)
x̄ = 25,1σ = 80
(viii)
x̄ = 3,1σ = 5
(ix)
x̄ = 4,1σ = 4
(x)
x̄ = 7,1σ = 5
(xi)
x̄ = 10,1σ = 12
LOI (%)
Depth (cm)
Rhyolitic shards/cm³
Rhyolitic shards/5 cm

Fig. 2

comparison, the data are shown alongside previous tephrostratigraphic results obtained from Loch an t'Suidhe (Roberts, 1999; Davies, 2002), Borrobol, Tynaspirit West and Whitrig Bog (Turney et al., 1997) as well as from a basin on Tanera Mor, in the Summer Isles, north-west Scotland (Roberts, 1997). The Vedde Ash, Ashik Tephra, Saksunarvatn Ash and Breakish Tephra are also present in a number of these sequences (Roberts, 1997; Turney et al., 1997; Roberts, 1999; Davies, 2002; Pyne-O'Donnell, in press), but only the Vedde Ash is shown in Fig. 2 in addition to the Interstadial ashes.

A discrete rhyolitic ash was detected in the approximate mid-Interstadial region of the Loch Ashik, Druim Loch, Loch an t'Suidhe and Borrobol sequences as reported in Pyne-O'Donnell (in press), where it has been named the Penifiler Tephra. It possesses a chemistry which is similar to the Borrobol Tephra (Fig. 3, Table 2). Additionally, two further occurrences of this ash may occur in the Tynaspirit West and Whitrig Bog sequences. EPMA analysis of the mid-Interstadial ash at Tynaspirit West (Fig. 2viii) (760-761 cm) is of Penifiler Tephra affinity, but the analytical totals for this sample fall just below the recommended 95% cut-off point for acceptable chemical data (Hunt and Hill, 1993). Nevertheless, this ash layer is provisionally assigned to the Penifiler Tephra on the basis of stratigraphic position and similarities in shard morphology. At Whitrig Bog a discrete ash peak is present in a mid-Interstadial stratigraphic position (Fig. 2xi) (205-210 cm), though shard numbers recovered were too low to enable chemical analysis. This layer is also assigned to the Penifiler Tephra because it occurs stratigraphically above a rhyolitic layer at the base of the Interstadial (275-280 cm) which Turney et al. (1997) assigned to the Borrobol Tephra, and hence is consistent with the other records shown in Fig. 2. The presence of the Borrobol

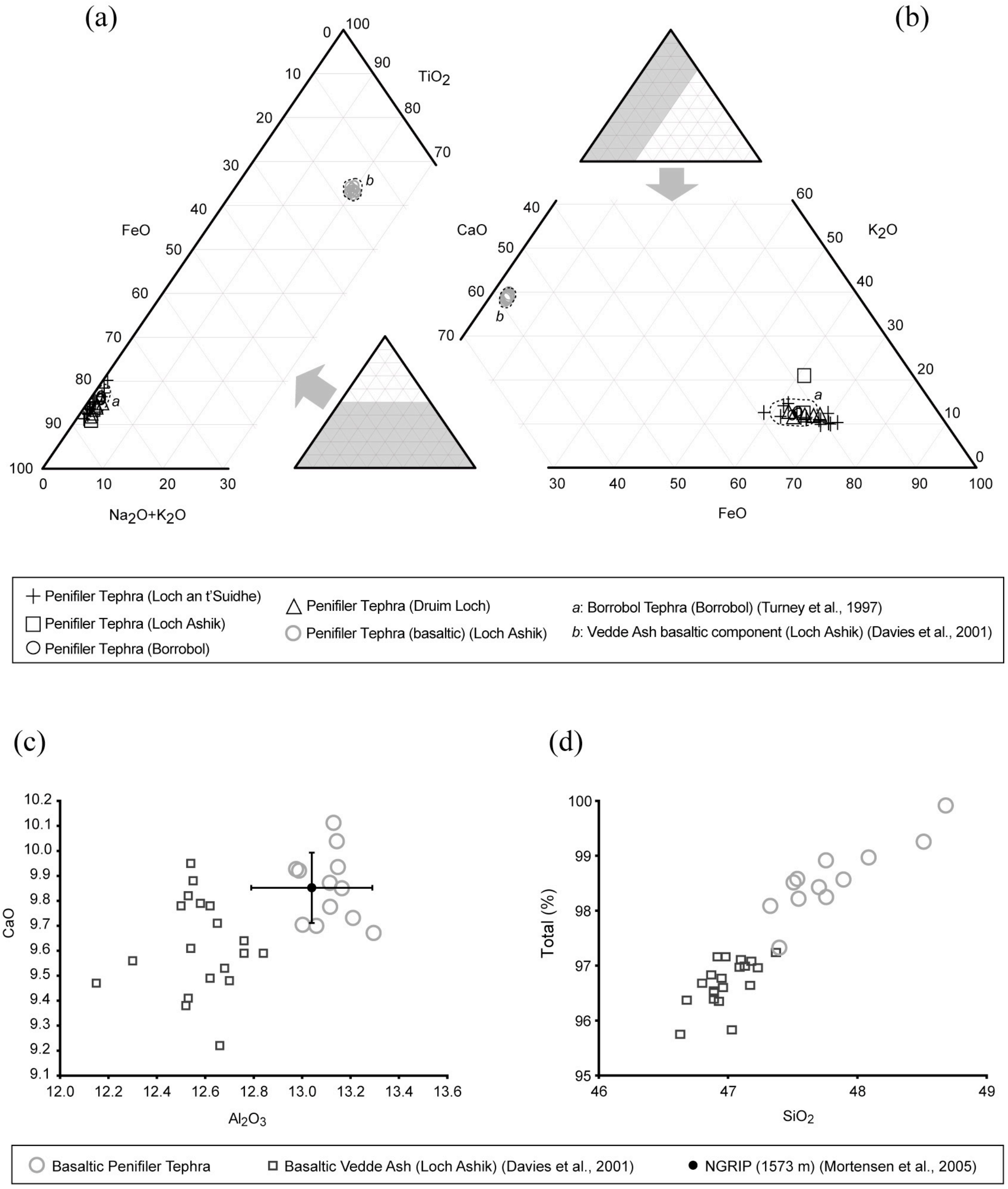
(a)
(b)
TiO2
FeO
Na2O+K2O
CaO
K2O
FeO
a
b
+ Penifiler Tephra (Loch an t'Suidhe)
□ Penifiler Tephra (Loch Ashik)
○ Penifiler Tephra (Borrobol)
△ Penifiler Tephra (Druim Loch)
○ Penifiler Tephra (basaltic) (Loch Ashik)
a: Borrobol Tephra (Borrobol) (Turney et al., 1997)
b: Vedde Ash basaltic component (Loch Ashik) (Davies et al., 2001)
(c)
CaO
Al2O3
(d)
Total (%)
SiO2
○ Basaltic Penifiler Tephra
□ Basaltic Vedde Ash (Loch Ashik) (Davies et al., 2001)
● NGRIP (1573 m) (Mortensen et al., 2005)

Fig. 3

Tephra in a number of the other sequences is also supported by chemical data reported by Roberts (1997) and Turney et al. (1997). An early Interstadial rhyolitic ash at Loch an t'Suidhe has also been tentatively attributed by Davies (2002) to the Borrobol Tephra (Fig. 2v). A number of shards from an early Interstadial layer at Loch an t'Suidhe were also analysed in Pyne-O'Donnell (in press) (Fig. 2iii; 661-662 cm), and while indicating a Borrobol Tephra affinity, analytical totals fell just below 95%. Until contradictory data are forthcoming, this layer at this site is assigned to the Borrobol Tephra on stratigraphic and morphological grounds, which are consistent with the other records in this study.

Magnetic separation of sediments containing the Penifiler Tephra at Loch Ashik revealed the presence of a large basaltic population accompanying the rhyolitic shards, with a maximum of ca. 1500 basaltic shards/cm^3. This basaltic population occurred in a central lake core (Fig. 5) and is different from that shown in Fig. 2i. The basaltic shard concentration maximum occurs at the same stratigraphic level as the rhyolitic component maximum (933 cm). The triplots in Fig. 3 show that on the basis of the major elements CaO, FeO and K_2O and FeO, total alkalis ($Na_2O + K_2O$) and TiO_2 the chemical signature of this basaltic population is similar to the basaltic component of the Vedde Ash (Mangerud et al., 1984; Birks et al., 1996), which also occurs at Loch Ashik in the GS-1 sediments (Davies et al., 2001). The dark-brown blocky shard morphology of the Penifiler Tephra basaltic population also resembles that of the Vedde Ash basaltic component. Comparison of CaO and Al_2O_3 concentrations between the two basaltic components, however, reveals a higher Al_2O_3 concentration for the Penifiler Tephra (Fig. 3c).

Fig. 2 shows that a consistent feature of the Borrobol Tephra is a stratigraphically diffuse distribution, rather than a single discrete narrow peak in shard concentration. In a number of the sequences the degree of shard dispersal is such that the distribution occupies a considerable proportion of the early Interstadial period around the shard maxima. This sometimes results in difficulty in identifying the initial ash deposition point in the stratigraphy for this isochron. Consistent shard morphology was observed in the Borrobol Tephra distributions examined in this study, suggesting it remains the same ash layer throughout. A number of the sequences also suggest the presence of two closely spaced, or stratigraphically bimodal, maxima in shard concentrations. This is best exhibited in the Loch an t'Suidhe (Fig. 2iii, iv and v) and Borrobol (Fig. 2vi and vii) records, with an absence of shards between the peaks in Fig. 2vii (Turney et al., 1997). Stratigraphic bimodality, however, is less evident within the diffuse Borrobol Tephra distributions in the remaining sequences depicted in Fig. 2.

4. Discussion

4.1. Stratigraphic distribution of the Borrobol Tephra

The findings reported above provide clear evidence for the existence of two distinct ash layers within the Lateglacial Interstadial, the mid-Interstadial Penifiler Tephra and the early Interstadial Borrobol Tephra, which have a similar chemistry. Furthermore, shard counts suggest a stratigraphic bimodality within the Borrobol Tephra in some of the sequences, which possibly results from more than one volcanic event, or alternatively the effects of sediment and shard reworking. These competing hypotheses are examined in this section.

It is reasonable to assume that ash dispersal and deposition will be heavily influenced by the climatic regime prevalent at the time. The observations of Mangerud et al. (1984) with respect to the distribution of the Vedde Ash provide a valuable comparison with the observed distributions of the Borrobol Tephra in the Scottish records. Mangerud et al. (1984) observed how harsh mid-GS-1 conditions and low catchment vegetation cover resulted in prolonged periods of Vedde Ash reworking from catchments into lakes. The Borrobol Tephra was deposited not long after GS-2 (Dimlington Stadial) ice retreat and would thus have been deposited onto catchment slopes which, like GS-1, were similarly poor in vegetation cover and with an abundance of loose sediment available for reworking into the lake. Shards of the Borrobol Tephra would thus have become mixed and entrained into this sediment and continually reworked into the lake until such time as the shards were depleted from the catchment or further sediment became unavailable for transport through slope stabilisation by vegetation development.

Such continual reworking of shards, in addition to producing a diffuse distribution, may also have been responsible for the stratigraphic bimodality seen in a number of the sequences in Fig. 2. It is possible that after vegetation development and reduced reworking, a short period of climatic deterioration may have led to increased shard inputs from the catchment resulting in a second ‘peak’. One such oscillation may be reflected in Fig. 2 by the short-lived decrease in LOI values labelled ‘a’, which may correspond with the ‘Older Dryas’/GI-1d cold interval (14 050 – 13 900 GRIP yrs BP) (Björck et al., 1998). An upper peak of reworked Borrobol Tephra may thus considerably post-date the initial ash deposition by ca. 500 yrs or more. Further comparison can be made with the distribution pattern of reworked Vedde Ash in Fig.

2, especially at Loch Ashik (Fig. 2i) and Borrobol (Fig. 2vii), which indicate how reworking can extend over prolonged periods to occupy the majority of the ca. 1000-year-long GS-1 stadial. If the upper peak of the Borrobol Tephra is the product of reworking, then only the lower peak can be considered as an isochron. Although not an isochron, an upper reworked peak may have value in delimiting the timing of the GI-1d oscillation on a regional basis.

The alternative hypothesis is that two volcanic events are represented by the Borrobol Tephra. Although some of the distribution patterns are suggestive of a double event, none, with the exception of the Borrobol site (Fig. 2g) (Turney et al., 1997), exhibit a distribution which is unambiguously resolvable into two truly discrete peaks. In the majority of cases there is a continual background of glass shards throughout these distributions, with peak maxima only slightly exceeding background concentrations. This is especially the case where shard numbers per cm^3 are low and where any peak may, therefore, arise merely by chance. In an attempt to define with more statistical rigour what constitutes a peak in these sequences, the mean and $+1\sigma$ have been calculated for all ash layer counts within GI-1 sediments in Fig. 2a. The results (Fig. 2b) show all peaks assigned to the Penifiler Tephra significantly exceed $+1\sigma$. The majority of Borrobol Tephra distributions also contain shard concentrations which exceed $+1\sigma$. However, only Loch an t'Suidhe core nt7 (Fig. 2biii) contains two clear peaks within the Borrobol Tephra distribution which exceed $+1\sigma$, with Borrobol Tephra distributions in the remainder of sequences falling at or below $+1\sigma$.

4.2. Chemical analysis of the Borrobol Tephra

The suspicion that the Borrobol Tephra comprised two minor peaks erupted in quick succession led Turney (1998b) and Roberts (1997) to test for chemical differences between both peaks at the sites of Borrobol and Tanera Mor respectively (Fig. 2vii and x). In both cases, no resolvable differences in EPMA chemistry were detected. This does little to resolve the issue, however, as only a marked difference in EPMA chemistry between the two peaks would eliminate one of the hypotheses. In any case, EPMA chemical analysis of the Borrobol and Penifiler ashes is problematic as glass shards in both contain large numbers of potassium feldspar microlite inclusions which contaminate the chemical signal of the pure glass and are difficult to eliminate, especially when analysing small shards. Alternative techniques to EPMA have been proposed which may provide more diagnostic information than major element ratios, for example, trace-element analysis by ICP-MS (Pearce et al., 2004) and SIMS (secondary ion mass spectrometry) (Bourdon et al., 1994; Corgne and Wood, 2004). The problem of microlite contamination, however, would remain (Pearce et al., 2002).

4.3. Radiocarbon dating of Interstadial Borrobol affinity ash layers

A number of radiocarbon ages with wide disparities have been reported for ashes with Borrobol chemical affinities. The ages derived from Lochan an Druim (Ranner et al., 2004) and Hässeldala port (Davies et al., 2004; Wohlfarth et al., 2006), for instance are anomalously young in comparison with the type site (Turney et al., 1997). While it is possible that these ashes may represent additional eruptions following the initial Borrobol Tephra deposition, it is possible that either ash may also represent the mid-Interstadial Penifiler Tephra. If this were the case then the stratigraphically lower Borrobol Tephra was either not deposited at these sites or was not preserved.

Table 4 shows a number of published ages for ashes of Borrobol affinity. These ages have been revised here using Bayesian modelling and the new IntCal04 calibration curve (Reimer et al., 2004). Despite these revisions, apparent differences in the reported ages for the Borrobol Tephra remain (Fig. 4) which may be explained by a reworked upper peak of the Borrobol Tephra or the presence of more than one ash of Borrobol affinity. There are also, however, inherent dating difficulties associated with two of the reported ages, at the type site and that of Ranner et al. (2005). The Turney (1998b) ages, from a bulk sample at the Borrobol type site, are misleadingly precise estimates because errors were not calculated on the original regression-based age model. Additionally, there is a reversal in the ages at the base of the sequence. The ages of the two ashes at 494 cm and 455 cm (Fig. 2vii) have been re-estimated here using a Bayesian sequence model with uniform prior assumptions and stratigraphically organised dates. Realistic errors can then be calculated for this site and calibrated with the IntCal04 calibration curve (Table 4).

The Ranner et al. (2005) age from north-west Scotland is also misleadingly precise. It is based on a third order polynomial regression equation through the mean point estimate of only five calibrated data points covering a period of ca. 7000 years. This approach is far from ideal when dealing with radiocarbon dates, where insufficient tie points will result in little better than millennial precision (Blockley et al., 2004; Telford et al., 2004). When the errors are accounted for, however, this age is consistent with the ages derived from Hässeldala port, in southern Sweden (Davies et al., 2004), though less precise. When comparing the new age model from Hässeldala port with the revised age for the younger (455 cm) ash at Borrobol a broad agreement can be seen between the two (Table 4) (Fig. 4).

Table 4

Site name	Calibrated age range (^{14}C yrs BP)	Calibration method	Author
Hässeldala port	14 450-13 800	Cariaco basin	Davies et al. (2004)
	14 331-13 667	Lake Suigetsu	Davies et al. (2004)
	14 013-13 713	IntCal04	Wohlfarth et al. (2006)
Borrobol (494 cm)	15 150-13 950	IntCal04	Turney (1998b) (revised)
Borrobol (455 cm)	13 840-13 440	IntCal04	Turney (1998b) (revised)
Lochan an Druim	13 610	Polynomial regression	Ranner et al. (2005)

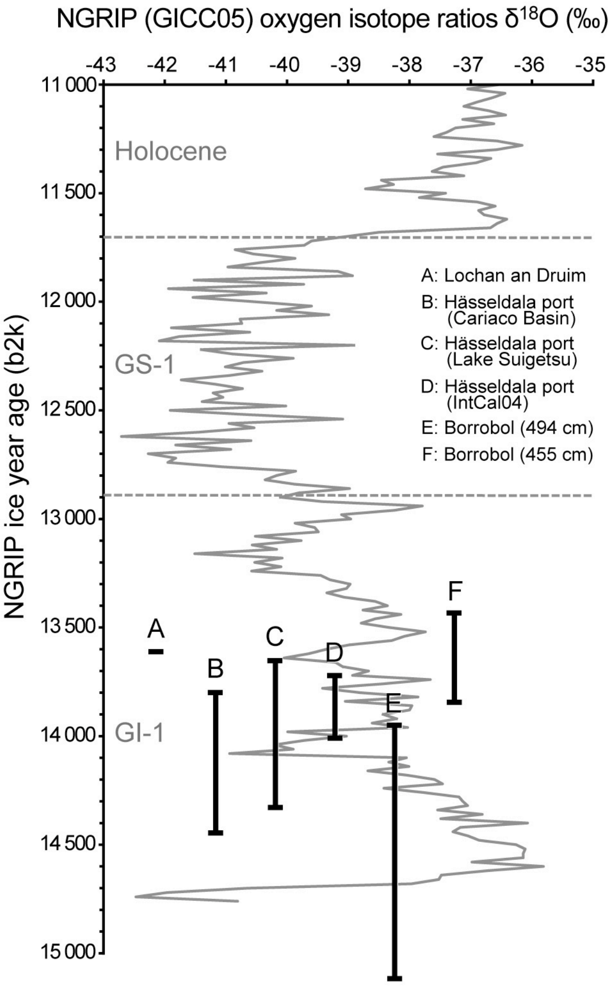
NGRIP (GICC05) oxygen isotope ratios δ18O (‰)
-43
-42
-41
-40
-39
-38
-37
-36
-35
NGRIP ice year age (b2k)
11 000
11 500
12 000
12 500
13 000
13 500
14 000
14 500
15 000
Holocene
GS-1
GI-1
A: Lochan an Druim
B: Hässeldala port (Cariaco Basin)
C: Hässeldala port (Lake Suigetsu)
D: Hässeldala port (IntCal04)
E: Borrobol (494 cm)
F: Borrobol (455 cm)
A
B
C
D
E
F

Fig. 4

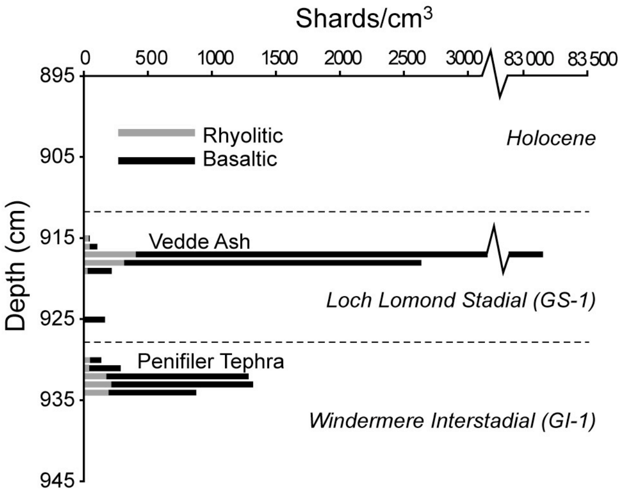
Shards/cm3
0
500
1000
1500
2000
2500
3000
83 000
83 500
Depth (cm)
895
905
915
925
935
945
Rhyolitic
Basaltic
Holocene
Vedde Ash
Loch Lomond Stadial (GS-1)
Penifiler Tephra
Windermere Interstadial (GI-1)

Fig. 5

Given the stratigraphic information from a number of the sites discussed above, it seems likely that there are at least two ashes of Borrobol affinity in the Lateglacial Interstadial. However, the many problems associated with the different radiocarbon ages still prevents a definitive dating of these layers.

4.4. A basaltic population accompanying the Penifiler Tephra

The occurrence of large numbers of basaltic shards accompanying the rhyolitic Penifiler Tephra at Loch Ashik (Fig. 5) suggests a basaltic population may accompany this ash. Given the nature of Icelandic volcanism this would not be surprising (Haflidason et al., 2000). Chemical analysis of the Penifiler Tephra basaltic population reveals it to be similar to the basaltic phase of the Vedde Ash, which also occurs at Loch Ashik (Davies et al., 2001), for the major elements shown in (Fig. 3). The Penifiler Tephra basaltic population shares similarly high titanium concentrations with the Vedde Ash, which is typical of eruptions associated with the Katla volcanic centre (Mangerud et al., 1984), although high titanium basalts have been associated with other Icelandic systems, albeit rarely. Recent results from the Greenland NGRIP ice-core reveals that numerous Icelandic eruptions with high titanium content chemistry, currently ascribed to the Katla system, are a feature of the Lateglacial eruptive history of Iceland (Mortensen et al., 2005). One basaltic ash layer in particular occurs at a stratigraphic depth of 1573 m. It possesses a very similar chemistry to the basaltic population reported here for the Penifiler Tephra (Fig. 3c; Fig. 5), with a similarly elevated aluminium content. This approximate GI-1c position in the NGRIP stratigraphy corresponds with the stratigraphic position of the Penifiler Tephra as indicated by LOI stratigraphy in a number of the sequences in Fig. 2. The 1573 m basaltic population has a NGRIP age of 14 040 b2k (before AD 2000)

(Rasmussen et al., 2006), which translates to 13 990 yrs BP (before 1950) with a maximum counting error of 182 years. This age conforms well to the Bayesian model age for the Hässeldala port Borrobol-like ash (Table 4) (Fig. 4).

Although the Penifiler Tephra basaltic population is most likely of Katla provenance, the chemistry of the rhyolitic population is very different from that of other rhyolitic materials attributed to this volcanic centre, for example, the Vedde Ash rhyolitic composition. The similarity of the Penifiler Tephra and Borrobol Tephra rhyolitic populations, however, suggests that they are both derived from the same volcanic centre (Fig. 3). This has been suggested by Davies et al. (2003) to possibly be Torfajökull or Snæfellsjökull, and by Haflidason et al. (2000) to be Hekla. The occurrence of the Penifiler Tephra rhyolitic and basaltic populations together at the same stratigraphic depth may, therefore, be the result of the separate but coincident eruptions of Katla and one of these other alkaline rhyolitic volcanic centres depositing both populations together. This hypothesis has been suggested by Larsen et al. (1999) for a number of Icelandic eruptions, whereby an eruption in one volcanic centre may trigger simultaneous eruptions in closely neighbouring systems.

In a number of the sequences examined in the course of this study, small numbers of hydrated basaltic shards were noted during rhyolitic shard extraction of the Borrobol Tephra. This suggests that a similar basaltic population may also exist for this ash in such lacustrine sequences. One sequence in particular to suggest this is Muir Park Reservoir in Perthshire, central Scotland, where the presence of the Borrobol Tephra has been provisionally identified by Cooper (1999). A core from this site (but different to that described by Cooper, 1999) was examined during the course of this study and a rhyolitic ash detected in the early Interstadial sediments, accompanied by basaltic shards. Unfortunately, subsequent attempts to constrain a more precise stratigraphic depth for this ash at 1 cm resolution, along with shard extraction for chemical analysis of the rhyolitic and basaltic populations, were unsuccessful.

5. Conclusion

This study presents findings from a number of sequences of varied origin which suggest the occurrence of a stratigraphic bimodality within the Borrobol Tephra. The firm presence of two early Interstadial eruptions, however, must await further verification at additional sites where their identity as discrete events can be untangled from the sedimentological and taphonomic issues. It is issues such as these which continue to prevent a satisfactory resolution of this question, despite a number of high-resolution Borrobol Tephra studies being conducted from a wide range of sites.

The confirmed presence of the new mid-Interstadial Penifiler Tephra in these sequences provides a useful isochron in this stratigraphic region. The possible presence of two discrete eruptions comprising the Borrobol Tephra would provide additionally useful isochrones in the early Interstadial period. To be useful as isochronous markers, however, deposition over a wide geographic extent is desirable. Thus far only the Scottish sequences described in this work have been shown to exhibit the mid-Interstadial Penifiler Tephra, along with the suggestion of a bimodal Borrobol Tephra.

The presence of a double Borrobol Tephra where there was previously one ash also presents difficulties in nomenclature with regard to which should be called the ‘Borrobol Tephra’. It is proposed here that if two discrete ash layers do indeed occur then they should both retain the name Borrobol Tephra, with the earlier being called Borrobol Tephra ‘A’ and the later Borrobol Tephra ‘B’.

Acknowledgements

Many thanks to the following people for their helpful advice and interpretation of results during the various stages of sample preparation and EPMA microprobe work: C.J. Doherty and C. Lane at The Research Laboratory for Archaeology and the History of Art (RLAHA), Oxford, and V. Hall, and S. McFarlan at the Electron Microscope Unit, Queen’s University Belfast. J. Mangerud and an anonymous reviewer are thanked for their constructive review comments. The results reported here are from the author's PhD programme of study, conducted at Royal Holloway, University of London under the supervision of John Lowe and Chris Turney, and are being extended within NERC RAPID Project (NE/C509158/1) ‘*Precise chronology of the timing of changes in behaviour of the North Atlantic THC and their forcing effects, 16-8 ka BP*’ which forms part of the NERC RAPID Climate Change Programme.

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Figure and Table captions

Fig. 1: Location map showing sample sites discussed in this study: (a) north-west Europe, British Isles and Scandinavia; (b) Scotland.

Fig. 2: (a) Loss on ignition (LOI) stratigraphy, ash shard concentration/cm^3 (not on same scale) and tephrocorrelations (grey shaded) for sites investigated in Pyne-O'Donnell (in press) (i, ii, iii, vi, viii) and Pyne-O'Donnell (2004) (xi), shown alongside sites selected from other published studies. Light dashed lines indicate the lower and upper boundaries of GS-1 (Loch Lomond Stadial/'Younger Dryas'). The broken sections of the Penifiler Tephra correlation indicate the estimated stratigraphic position of this ash in sequences where it has not yet been detected. Where investigated, the mid-GS-1 Vedde Ash is also shown in light grey with maximum shard concentration number indicated in brackets. The LOI oscillations marked 'a' and 'b' in GI-1 sediments possibly correspond with the Older Dryas (GI-1d) (14 050-13 900 GRIP yrs BP) and Killarney-Gerzensee Oscillation or Intra-Allerød Cold Phase (IACP) (GI-1b) (13 150-12 900 GRIP yrs BP) periods respectively. Borrobol Tephra distributions with pronounced stratigraphic bimodality are marked by black arrows. (b) Interstadial ash shard concentrations as in (a) shown with mean ($\bar{x}$) (black dashed line) and plus one standard deviation (+1σ) over mean (grey shaded region). Only sequences containing both Borrobol and Penifiler ashes together are shown. Published source sequences from: (iv) Roberts (1999), (v) Davies (2002), (vii and ix) Turney et al. (1997) and (x) Roberts (1997).

Fig. 3: Triplots and biplots of major oxide concentrations for ashes found at study sites: (a) FeO, total alkalis (Na_2O+K_2O) and TiO_2; (b) CaO, FeO and K_2O; (c) Al_2O_3 and CaO; (d) SiO_2 and analytical totals (%). The chemical envelopes of the Borrobol Tephra at the type site and Vedde Ash (basaltic component) at Loch Ashik are also shown for comparison.

Fig. 4: Borrobol Tephra age ranges (A – F) from Table 4 compared with Greenland NGRIP δ^{18}O oxygen isotope ratios (‰) from GICC05 time scale with 20 year means. Note Lochan an Druim age is represented as a single point only as error ranges are not calculated. Light dashed lines indicate the lower and upper boundaries of GS-1 (Loch Lomond Stadial/'Younger Dryas'). NGRIP oxygen isotope data and lithological divisions from Rasmussen et al. (2006) and official NGRIP web page.

Fig. 5: Rhyolitic and basaltic shard concentrations for the Vedde Ash and Penifiler Tephra at Loch Ashik core location Isl-W. Light dotted lines indicate the lower and upper boundaries of GS-1 (Loch Lomond Stadial/'Younger Dryas').

Table 1: Location of sites discussed in this study. Sample type and basin and drainage area are also shown. Basin and drainage area estimates for Druim Loch, Borrobol, Tynaspirit West and Whitrig Bog are from Dadswell (2002) and Turney (1998b).

Table 2: Major oxide concentrations (wt %) of individual shards from ash layers at study sites. Mean and one standard deviation (1σ) are shown, with total iron expressed as FeO. (a): Analyses performed at The Research Laboratory for

Archaeology and the History of Art (RLAHA), Oxford; (b): analyses performed at the Electron Microscope Unit at Queen's University, Belfast.

Table 3: Lipari secondary standard block summary results for ash analyses conducted on the Oxford microprobes. Results show mean and one standard deviation (1σ) for the standard measurements taken during the course of ashes analysed in Table 2, compared to the expected results based on repeat analyses of this block. Also shown are the results of analyses at Oxford of a block from the Lipari flow published in Hunt and Hill (1996, 2001), kindly provided by J.B. Hunt to test the initial operating conditions of the Oxford microprobes.

Table 4: Reported radiocarbon ages for ashes of Borrobol affinity (not including Penifiler Tephra) from: Hässeldala port (Sweden) (Davies et al., 2004; Wohlfarth et al., 2006), Borrobol (Scotland) (Turney, 1998b) and Lochan an Druim (Scotland) (Ranner et al., 2005). Ages have been revised here using Bayesian modelling and calibration by the IntCal04 calibration curve of Reimer et al. (2004).