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First identification and characterization of Borrobol-type tephra in the Greenland ice cores: new deposits and improved age estimates

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ABSTRACT: Contiguous sampling of ice spanning key intervals of the deglaciation from the Greenland ice cores of NGRIP, GRIP and NEEM has revealed three new silicic cryptotephra deposits that are geochemically similar to the well-known Borrobol Tephra (BT). The BT is complex and confounded by the younger closely timed and compositionally similar Penifiler Tephra (PT). Two of the deposits found in the ice are in Greenland Interstadial 1e (GI-1e) and an older deposit is found in Greenland Stadial 2.1 (GS-2.1). Until now, the BT was confined to GI-1-equivalent lacustrine sequences in the British Isles, Sweden and Germany, and our discovery in Greenland ice extends its distribution and geochemical composition. However, the two cryptotephra deposits that fall within GI-1e ice cannot be separated on the basis of geochemistry and are dated to 14358±177 a 2σ b2k and 14252±173 a 2σ b2k just 125±3 years apart. The older deposit is consistent with BT age estimates derived from Scottish sites, while the younger deposit overlaps with both BT and PT age estimates. We suggest that either the BT in Northern European terrestrial sequences represents an amalgamation of tephra from both of the GI-1e events identified in the ice-cores or that it relates to just one of the ice-core events. A firm correlation cannot be established at present due to their strong geochemical similarities. The older tephra horizon, found within all three ice-cores and dated to 17326±319 a 2σ b2k, can be correlated to a known layer within marine sediment cores from the North Iceland Shelf (ca. 17179-16754 cal a BP). Despite showing similarities to the BT, this deposit can be distinguished on the basis of lower CaO and TiO2 and is a valuable new tie-point that could eventually be used in high-resolution marine records to compare the climate signals from the ocean and atmosphere.

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KEYWORDS: Borrobol; cryptotephra; Greenland ice cores; isochron; Penifiler.

Introduction

Tephrochronology has long been established as a tool that exploits ash deposits with unique geochemical fingerprints to precisely correlate a diverse range of palaeoarchives from widely separated localities (e.g. Lowe, 2011). Tephra deposits are preserved in a wide range of depositional environments including marine, ice and terrestrial records and thus have the potential to give rise to valuable time-synchronous horizons (e.g. Lane et al., 2013). Over the last few decades, the scope of this technique has changed considerably through the investigation of cryptotephra deposits that are invisible to the naked eye and can only be detected by employing microscopy techniques (e.g. Davies, 2015). Cryptotephra investigations in Greenland have highlighted the value of polar ice cores as volcanic ash repositories and the potential of bearing isochronous horizons for synchronizing the ice to other palaeoarchives (e.g. Grönvold et al., 1995; Mortensen et al., 2005; Davies et al., 2008, 2010; Abbott and Davies, 2012; Bourne et al., 2015, 2016).

Many Late-glacial tephra deposits identified in European terrestrial records, however, have not yet been identified in the ice. Here we target our searches to identify the Borrobol (BT) and Penifiler (PT) cryptotephra in the Greenland ice cores. Both are distinguishable from other Late-glacial cryptotephra deposits by low FeO and TiO2 and high MnO content and are found exclusively in terrestrial deposits in the North Atlantic (NA) region. The BT and PT are close in age and composition and, as a result, present problems for correlation purposes (see Lind et al., 2016 for a summary of BT and PT findings in NA records). The BT was first identified in three Scottish palaeolakes, Borrobol Bog, Tynaspirit West and Whitrig Bog by Turney et al. (1997) in early Late-glacial Interstadial sediments [probably analogous to Greenland Interstadial 1e (GI-1e) in Greenland or Bølling in Scandinavia] and was subsequently thought to have been identified at Håsseldala port and Skallahult in Sweden by Davies et al. (2003) (see Fig. 1 for site locations). However, with a new pollen stratigraphy and age estimates, Davies et al. (2004) showed that the horizon identified in Håsseldala port is associated with Older Dryas sediments (probably analogous to the short-lived GI-1d cold event in Greenland). This discovery was inconsistent with the Scottish occurrences that were associated with older Late-glacial interstadial sediments (analogous to the warmer GI-1e) and prompted Davies et al. (2004) to propose that two tephras with identical geochemistry were deposited during GI-1. Further evidence to support this was presented by Pyne-O’Donnell (2007) and Pyne-O’Donnell et al. (2008) who revisited the Scottish palaeolakes investigated by Turney et al. (1997) and identified two closely spaced horizons with an identical composition to the BT. The

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deposits were positioned in what were described by the authors as early- and mid-interstadial sediments (Fig. 2) and they recommended that the older deposit should be considered the BT, as defined by Turney et al. (1997), while the younger deposit was named the PT. Subsequent work by Matthews et al. (2011) outlined new radiocarbon age estimates for the BT and PT horizons based on their positions and, more importantly, chironomid-inferred temperature estimates for the BT and PT based on pollen evidence and stratigraphic position, but this cannot be proven given the overlap between BT and PT age estimates (Bronk Ramsey et al., 2015). Furthermore, new trace element comparisons of the BT, extracted from a new core from the Borrobol site and (presumably) the PT from these records such as Hörvåg and Skallahult; Davies et al., 2003, 2004; Lind et al., 2016). Current thinking suggests a correlation between the Swedish deposits and the PT based on pollen evidence and stratigraphic position, but this cannot be proven given the overlap between BT and PT age estimates (Bronk Ramsey et al., 2015). Furthermore, new trace element comparisons of the BT, extracted from a new core from the Borrobol site and (presumably) the PT from these Swedish sites found that the deposits were indistinguishable from each other (Lind et al., 2016).

To complicate matters, individual deposits in marine cores HM107-05 (382–379 cm), MD99-2275 (3679 cm) and MD99-2271 (806–808 cm) from the North Iceland shelf have been discovered by Eriksson et al. (2000), Søndergaard (2005) and Gudmundsdottir et al. (2011, 2012), respectively. All cores have been correlated to each other by Gudmundsdottir et al. (2012) using magnetic susceptibility and isotope profiles and the tephra deposits found were originally correlated to the BT
based on geochemical similarities (i.e. Halldason et al., 2000; Gudmundsdóttir et al., 2011, 2012). However, all tephra deposits are in fact associated with glacial sediments, stratigraphically located below Bølling or GI-1-equivalent tephra deposits are in fact associated with glacial sediments, (2013) and the best available AMS14C age estimate is benthic foraminifera. Similarly, a Borrobol-type tephra was yet Eríksson/C19/C6 based on geochemical similarities (i.e. Haflidason standard reservoir correction of 400 years to their14Cd a te s, both Jarvis (2013) and Eríksson/ottir et al. (2004) noted that the temporal variability in radiocarbon age estimates was first noted by Lowe (2001). and this discrepancy between terrestrial and marine-based chronological evidence therefore indicates that the marine deposits found in terrestrial and marine sediments (e.g. Gudmundsdottir et al., 2011, 2012; Matthews et al., 2011; Brooks et al., 2016) is shown for context. References for all sites containing these horizons are given in Fig. 1.

**Methodology**

**Ice-core sampling**

Three Greenland ice-cores (NGRIP, GRIP and NEEM) were used to search for the BT, PT and the older Borrobol-type tephras between GS-2.1 and GI-1. The timing of Greenland interstadials (GI) and stadials (GS) and ages presented in this study have been defined by Greenland Ice Core Chronology 2005 (GICC05) (Andersen et al., 2006; Rasmussen et al., 2006, 2014; Seierstad et al., 2014) and GICC05modelext-NEEM-1 (Rasmussen et al., 2013). The GICC05 multi-core (NGRIP, DYE-3, GRIP) timescale was constructed by counting annual layers back from 2000 AD (b2k) using multiple parameters (e.g. δ18O, calcium ions) and uncertainty is based on a maximum counting error (MCE) of ambiguous layers, equivalent to 2σ, where cumulative errors increase with depth (Andersen et al., 2006; Rasmussen et al., 2006). NGRIP and GRIP ice samples were selected to encompass mid-GI-1e through to early GI-1c ice (Fig. 2) to maximize the chances of isolating the BT and PT. The GI-1 sampling strategy for NEEM was based on coarse-resolution screening of meltwater samples (1.1 m) derived directly from the continuous flow analysis (CFA) system (Bigler et al., 2011) for the entire interstadial and high-resolution sampling was informed by the age estimates of Matthews et al. (2011) and GICC05modelext-NEEM-1, which encompassed mid- to late GI-1e and the complete GI-1d (Fig. 2). To trace the older GS-2.1-equivalent Borrobol-type tephra, coarse-resolution CFA samples from NEEM were screened and used to inform a higher-resolution
sampling strategy for NEEM, NGRIP and GRIP (Fig. 2). All ice sampling was contiguous to maximize cryptopetra extraction. Ice cores are cut into sections of 55-cm length in the field, and a 2-cm³ section of ice was cut from the outer edge of each 55-cm section and further subsampled at a resolution of 15–20 cm. Individual samples were melted and centrifuged in tubes for 5 min at 2500 r.p.m. and at the end of this process any particulate matter, including tephra, remained concentrated at the bottom of the tubes. Supernatant water was discarded, leaving 2–3 mL of sample that was evaporated onto a frosted glass microscope slide and covered in epoxy resin for optical assessment, using high-magnification light microscopy. Slides containing tephra were selected for electron probe micro-analysis (EPMA).

Geochemical analysis

EPMA by wavelength dispersive spectrometry (WDS) is the preferred method for major element characterization of individual tephra grains and requires flat exposed sections through grains for electron bombardment and X-ray generation (Hunt and Hill, 1993; Hayward, 2012). To obtain these thin sections, epoxy resin was ground down using electrocoated silicon carbide paper and then polished using 6-, 3- and 1-µm diamond suspension and 0.3-µm alumina micro polish. EPMA was performed using a Cameca SX100 electron probe micro-analyser at the Tephra Analysis Unit, University of Edinburgh. This system has five wavelength dispersive spectrometers and was calibrated daily using internal calibration standards as described by Hayward (2012) and secondary standards were analysed daily and monitored to identify instrumental drift. Major element and secondary standard concentrations are provided in Supporting Information, Table S1.

Trace element analyses were performed on the same glass shards that had been analysed for major elements, using laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) at the Department of Geography and Earth Sciences, Aberystwyth University. Here a Coherent GeoLas ArF 193 nm Excimer LA system was operated with a fluence of 10 J cm⁻² at a repetition rate of 5 Hz. The analyses were performed using 10-µm ablation craters, with spectra collected for a 24-s acquisition on a Thermo Finnigan Element 2 sector field ICP-MS. The minor ²⁹Si isotope was used as the internal standard (using the anhydrous, normalised SiO₂ from EPMA) with the NIST 612 reference glass used for calibration, taking concentrations from Pearce et al. (1997). A fractionation factor was applied to the data to account for analytical bias related to the different matrices of the reference standard and the sample. Data were filtered for inclusion of phenocryst phases to leave only glass analyses. Full details of these methods as well as LA-ICP-MS operating conditions are given in Pearce et al. (2011) and Pearce (2014) and trace element concentrations are provided in Table S2.

Results

Tephra deposits were identified within GI-1e and GS-2.1 ice. Despite sampling the entire GI-1d cold event in three ice cores no colourless glass shards consistent with the BTP/T were identified. Other stratigraphically significant cryptopetras were identified within these sampling windows (Fig. 2), some of which were used by Seierstad et al. (2014) for the timescale transfer of GICC05 to GRIP; however, this work focuses only on the Borrobol-type horizons and the full tephrostratigraphy will be reported elsewhere.

Tephra in GI-1e ice: stratigraphic position and geochemical composition

Two individual cryptopetra deposits composed of colourless/pinkish shards with distinctive fluted/cuspate morphology were identified in GI-1e in GRIP and one deposit in NGRIP (Fig. 2, Table 1). The older of the two GRIP deposits was found at 1734 m depth (14 358 ± 177 a b²k or 14 308 ± 177 a b²k) and the younger was found at 1727.75 m depth (14 252 ± 173 a b²k or 14 202 ± 173 a b²k). The single GI-1e deposit in NGRIP was found at a depth of 1582.75 m (14 252 ± 173 a b²k or 14 202 ± 173 a b²k). No rhyolitic material was identified in NIEEM in the targeted GI-1e-d sampling window. Major element analyses (Table 2) show a near identical composition between all these layers which all have a homogeneous population that spans the boundary between low- and high-alcali rhyolites (Fig. 3A,B). The total alkalai (TA) content (Na₂O + K₂O) ranges between 7.69 and 8.55 wt%, the SiO₂ values range between 75.90 and 77.40 wt%, and the FeO and TiO₂ contents are between 1.20 and 1.83 wt% and 0.08 and 0.19 wt%, respectively (Table 2; Supporting Table S1; Fig. 3A–C). Statistical analysis of GI-1e sample pairs found in NGRIP (1582.75 m) and GRIP (1727.75 and 1734 m) supports a common origin from a single volcano, based on high similarity coefficients (SC between 0.979 and 0.981) and low D² values between 0.280 and 1.088, far below the D⁰critical value of 18.46 at the 99% confidence level.

The Icelandic system producing Borrobol-type material remains unknown (Lind et al., 2016) and our major element comparisons indicate that this tephra has no consistent

Table 1. Summary information for Borrobol-type tephra deposits from GI-1e and GS-2.1 including the ice-core depth interval (metres) within which each deposit was found and a Greenland Ice Core Chronology 2005 (GICC05) age (using the lower ice depth age). Age uncertainty is based on ‘uncertain annual layers’ and for N uncertain layers the error = N x 0.5 years, and the accumulated error is obtained by summing these layers and is called the maximum counting error (MCE), equivalent to 2σ (Andersen et al., 2006; Rasmussen et al., 2006). For NIEEM, a GICC05 age has been assigned to the GS-2.1 deposit 1524.80 m as it can be correlated to the NGRIP deposit at 1665.60 m. Geochemical composition, shard concentrations and average shard size are provided. The Rock type classification is based on Le Maitre (2002). EPMA conditions were optimized for analysis of small cryptopetra grains (<20 µm diameter) and samples in this study were analysed with either a 5- or 3-µm beam diameter using the operating conditions outlined in Hayward (2012).

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth (top) (m)</th>
<th>Depth (bottom) (m)</th>
<th>Max. age (a b²k) and MCE</th>
<th>Composition</th>
<th>Grain count</th>
<th>Grain size: long axis (µm)</th>
<th>EPMA beam size (µm)</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>NGRIP</td>
<td>1582.55</td>
<td>1582.75</td>
<td>14 252 ± 173</td>
<td>Rhyolite</td>
<td>86</td>
<td>30.5</td>
<td>3</td>
<td>GI-1e</td>
</tr>
<tr>
<td>GRIP</td>
<td>1727.55</td>
<td>1727.75</td>
<td>14 252 ± 173</td>
<td>Rhyolite</td>
<td>102</td>
<td>33.1</td>
<td>5</td>
<td>GI-1e</td>
</tr>
<tr>
<td>GRIP</td>
<td>1733.80</td>
<td>1734.00</td>
<td>14 358 ± 177</td>
<td>Rhyolite</td>
<td>93</td>
<td>34.3</td>
<td>3</td>
<td>GI-1e</td>
</tr>
<tr>
<td>NGRIP</td>
<td>1665.40</td>
<td>1665.60</td>
<td>17 326 ± 319</td>
<td>Rhyolite</td>
<td>&gt;2000</td>
<td>47.4</td>
<td>5</td>
<td>GS-2.1</td>
</tr>
<tr>
<td>GRIP</td>
<td>1818.15</td>
<td>1818.30</td>
<td>17 326 ± 319</td>
<td>Rhyolite</td>
<td>431</td>
<td>49.4</td>
<td>5</td>
<td>GS-2.1</td>
</tr>
<tr>
<td>NEEM</td>
<td>1524.60</td>
<td>1524.80</td>
<td>17 326 ± 319</td>
<td>Rhyolite</td>
<td>124</td>
<td>36.8</td>
<td>5</td>
<td>GS-2.1</td>
</tr>
</tbody>
</table>

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Table 2. Mean major and trace element values for each tephra deposit with associated standard deviations (1 or 2σ). Major elements were obtained by EPMA of individual grains and mean anhydrous (norm) values are expressed as weight% of sample, together with average values of raw (hydrous) totals. The ice-core sample depth and the number of analyses (n) are given for each deposit. All analyses were performed at the Tephra Analysis Unit (TAU), University of Edinburgh, using a Cameca SX100 electron microprobe. Trace element data are expressed in parts per million. All samples were analysed by LA-ICP-MS at the University of Aberystwyth with a 10-μm beam spot size using a Coherent Geolas ArF 193-nm Eximer laser ablation unit coupled to a Thermo Finnigan Element 2 high-resolution sector mass spectrometer. The USGS reference glass MD99-2271 is included for quality assurance.

<table>
<thead>
<tr>
<th>Tephra deposit</th>
<th>Mean</th>
<th>2σ (n = 6)</th>
<th>Mean (n = 7)</th>
<th>2σ (n = 7)</th>
<th>Mean (n = 8)</th>
<th>2σ (n = 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRIP 1727.75 m</td>
<td>76.37</td>
<td>0.94</td>
<td>76.48</td>
<td>0.80</td>
<td>76.42</td>
<td>1.18</td>
</tr>
<tr>
<td>GRIP 1734 m</td>
<td>0.12</td>
<td>0.02</td>
<td>0.11</td>
<td>0.04</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>NGRIP 1665.60 m</td>
<td>12.89</td>
<td>0.75</td>
<td>12.61</td>
<td>0.50</td>
<td>12.64</td>
<td>1.14</td>
</tr>
<tr>
<td>GRIP 1818.30 m</td>
<td>1.52</td>
<td>0.26</td>
<td>1.46</td>
<td>0.76</td>
<td>1.47</td>
<td>0.31</td>
</tr>
<tr>
<td>NEEM 1524.80 m</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>MD99-2271</td>
<td>3.90</td>
<td>0.19</td>
<td>3.95</td>
<td>0.22</td>
<td>3.99</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Major elements

- **SiO2**
- **TiO2**
- **Al2O3**
- **FeO**
- **MnO**
- **MgO**
- **K2O**
- **Na2O**
- **CaO**
- **MnO**
- **SiO2**
- **Ba**
- **Cs**
- **Cl**

Trace elements

- **Rb**
- **Sr**
- **Y**
- **Zr**
- **Nb**
- **Cs**
- **Ba**
- **Nd**
- **Sm**
- **Eu**
- **Gd**
- **Tb**
- **Dy**
- **Ho**
- **Er**
- **Tm**
- **Yb**
- **Lu**
- **Hf**
- **Ta**
- **Th**
- **U**
- **Pb**

Table 3: Mean major and trace element values for each tephra deposit with associated standard deviations (1 or 2σ). Major elements were obtained by EPMA of individual grains and mean anhydrous (norm) values are expressed as weight% of sample, together with average values of raw (hydrous) totals. The ice-core sample depth and the number of analyses (n) are given for each deposit. All analyses were performed at the Tephra Analysis Unit (TAU), University of Edinburgh, using a Cameca SX100 electron microprobe. Trace element data are expressed in parts per million. All samples were analysed by LA-ICP-MS at the University of Aberystwyth with a 10-μm beam spot size using a Coherent Geolas ArF 193-nm Eximer laser ablation unit coupled to a Thermo Finnigan Element 2 high-resolution sector mass spectrometer. The USGS reference glass MD99-2271 is included for quality assurance.

- **SiO2**
- **TiO2**
- **Al2O3**
- **FeO**
- **MnO**
- **K2O**
- **Na2O**
- **CaO**
- **MgO**
- **SiO2**
- **Ba**
- **Cs**
- **Cl**

Both GRIP GI-1e deposits geochemically match the NGRIP GRIP 1727.75 m, and GRIP 1734 m, were matched and thus trace the common age of 14 252 ± 173 a B2k and also occupy a stratigraphic position approximately 200 years before the start of GI-1d. GRIP 1734 m is 106 ± 3 years older (14 358 ± 177 a B2k) and is found in the middle of the GI-1e warm event, immediately before a gradual downturn trend in surface air temperature according to the δ18O record (Fig. 2) (NGRIP Members, 2004).

Single-shards were analysed by LA-ICP-MS (Table 2) and when average rare earth element (REE) profiles are displayed together with the individual grain analyses, there is a general similarity between all layers from GI-1e (Fig. 3D). The REE profiles appear typical of Icelandic rhyolitic products.
Figure 3. (A) Normalized glass analyses from three GI-1e and three GS-2.1 ice core deposits, plotted against rock type, which is assigned on the total alkali vs. silica content (TAS) (Le Bas et al., 1986). Data are normalized to an anhydrous basis (i.e. 100% total oxides) following the recommendation of Pearce et al. (2014). (B) Compositional envelopes for identifying tephra provenance of Icelandic silicic tephra layers using major elements. The diagram is adapted from Meara (2012) with data for Eyjafjallajökull and Snæfellsjökull volcanic systems sourced from Larsen et al. (1999) and Jonasson (2007). The low and high alkali boundary is based on Jonasson (2007). (C) Comparison of the GI-1e and GS-2.1 ice core deposits relative to the compositional envelope for the BT and PT are constructed using data from Turney et al. (1997), Pyne-O’Donnell (2007), Pyne-O’Donnell et al. (2008), Matthews et al. (2011) and Lind et al. (2016). This comparison highlights the difference in CaO and TiO2 in the GS-2.1 ice-core tephras. Error bars represent two standard deviations (2σ) of replicate analyses of the Lipari obsidian secondary standard; grey bars correspond to GI-1e samples and blue to GS-2.1 samples. (D and E) Chondrite-normalized REE profiles for individual grains from GI-1e and GS-2.1 deposits respectively. The chondrite composition is from McDonough and Sun (1995) and thick blue bars represent end member characterizations of Icelandic rhyolites, reported in Oskarsson et al. (1982).
based on a comparison with end-member characterizations of Icelandic rhyolites from Öskarsson et al. (1982) (Fig. 3D). This includes high absolute concentrations of Sr, Zr and Ba, light REE (LREE) enrichment (La to Nd >100 times the chondritic value) with a profile that slopes steeply down to the pronounced negative anomaly of Eu, indicating feldspar fractionation. The steep profile of these incompatible LREEs gives way to a flat profile that characterizes the abundance of middle REEs (MREEs) and heavy REEs (HREEs) between Gd and Lu. The range of concentrations and element ratios, e.g. Ce/Yb (Fig. 4) are the same for sample pairs GRIP 1727.75 m and NGRIP 1582.75 m, and also GRIP 1734 m, although not identical in terms of REE, with the NGRIP sample looking to be more evolved than GRIP 1727.75 m, based on higher REE abundance. It must be emphasized that only a small number of analyses were possible on the Greenland ice-core samples (Table 2) and these may only represent part of the eruption’s compositional range, with the possibility that further analyses could extend the fields of data. When coupled with the analytical noise for analyses performed at 10 µm, close to the limit of the LA-ICP-MS method, it should be noted that the data will be influenced by larger uncertainties that do not typically hamper analyses of larger particles. Statistical analysis of 15 trace elements from deposits NGRIP 1582.75 m and GRIP 1727.75 m (that form the younger GI-1e horizon) produces a $D^2_{critical}$ value of 3.506, which is below the critical value of 30.58 at the 99% confidence level and demonstrates that the geochemical composition is not significantly different.

**Geochemical and chronological comparison to other North Atlantic Borrobol-type deposits in GI-1e**

The two ice-core tephra horizons fall within the BT/PT compositional envelope (Fig. 3C) and the best geochemical...
matches are with the new data-sets (BT: BO521 and PT: BO486) from the original Borrobol site published in Lind et al. (2016) (Fig. 4A–C). Older data have a consistently lower Na2O content, typically ~0.65 wt% less than the ice-core results. The offset is probably due to sodium loss in older analyses and the similarities between our data and the Lind et al. (2016) analyses could be because they were both analysed with improved conditions and EPMA modification, described by Hayward (2012). There is consistent major element overlap between the ice-core data and BO521 and BO486 and all exhibit the trend of evolution by fractionation of feldspar (Fig. 4B), which is typical for Icelandic rhyolites (SiO2 increases as CaO and Al2O3 decrease). Lind et al. (2016) have assumed BT and PT ages from Bronk Ramsey additional analyses are required to explore this further.

Tephra in GS-2.1 ice; stratigraphic position and geochemical composition

Three deposits were identified within GS-2.1 ice in the following samples: NEEM 1524.80 m, NGRIP 1665.60 m and GRIP 1818.30 m (Table 1) and contain high concentrations of colourless glass shards. The ages of the deposits are consistent between cores and the NGRIP 1665.60 m/GRIP 1818.30 m match-point is included within an NGRIP/GRIP timescale synchronization performed by Seierstad et al. (2014). While the GICC05 age for this GS-2.1 deposit is 17 326 ± 319 a BP (17 276 ± 319 a BP), the age according to the first NEEM timescale is 17 386 ± 173 a BP (GICC05modNeem-NEEM-1). However, this new deposit sits along a trend line (Fig. 5) when plotted together with the depths of NEEM/NGRIP

Figure 5. Individual ECM match points between NEEM and NGRIP over the interval of GS-1 to GS-3, highlighting a wide gap in GS-2.1 chemostratigraphic matching (Rasmussen et al., 2013). The new GS-2.1 Borrobol-type match-point NEEM 1524.80 m/NGRIP 1665.60 m is shown within this gap.
All deposits have an identical rhyolite major element composition (Table 2, Fig. 3A,B) and are almost identical in composition to the GI-1e ice-core deposits. It is apparent, however, that there are consistent differences in the CaO and TiO$_2$ values that discriminate between the GS-2.1 and GI-1e deposits (Fig. 3C). Statistical analyses of major elements support a correlation between the NGRIP, GRIP and NEEM deposits with SC values ranging between 0.988 and 0.995 and $D^2$ values ranging between 0.240 and 1.100, strongly suggesting a compositional/genetic link between the deposits.

The average REE profiles of the GS-2.1 deposits fall within boundaries of typical Icelandic rhyolitic products and are very similar with a particularly good agreement between the incompatible LREE and MREE profiles, including a pronounced negative Eu anomaly (Fig. 3E). There is more variability between individual analyses of HREEs because of the low concentrations of these elements, which are close to variability between individual analyses of HREEs because of the low concentrations of these elements, which are close to

Geochemical and chronological comparison to other North Atlantic Borrobol-type deposits in GS-2.1

The GS-2.1 ice-core horizon has potential counterparts in the marine realm, with four similar Borrobol-type deposits found in glacial (GS-2.1 equivalent) sediments. The best (reservoir-corrected) age estimate for this marine isochron is 17 179–16 754 cal a BP (Jarvis, 2013) and is comparable to the ice-core age of 17 276±319 a BP. Furthermore, major element comparisons between the ice-core deposits and MD99-2271 (newly acquired data for this study, Table 2), MD99-2272 and MD99-2275 (Table S1) shows good agreement between the datasets (Fig. 6). This relationship is supported by statistical analyses, particularly with MD99-2271, which has an SC of 0.99 and a $D^2$ of 2.07 and can be interpreted as a volcanic event match as well as a provenance match. SC and $D^2$ values of 0.95 and 4.32, respectively, also support a common volcanic source between the ice-core deposits and MD99-2272 (Table 3), although there is an observed Na$_2$O offset that probably reflects sodium loss during EMPA (Fig. 6A). A similar offset is observed in data from MD99-2275 grains, which otherwise compares well to the ice-core data (Fig. 6B,C). However, with just three analyses from this deposit and low oxide totals, statistical comparison could not be performed with confidence.

Discussion

Three cryptotephra deposits with a Borrobol-type composition have been identified for the first time in Greenland ice spanning GS-2.1 (one horizon) and GI-1e (two horizons), but Borrobol-type deposits were absent from GI-1d ice. For the two compositionally identical events, ca. 106 years apart in GI-1e ice, the correlation issues that plague the BT remain. Without any diagnostic geochemical features, pinpointing a correlation to either the BT or the PT in terrestrial sequences is limited. Our new trace element data show some tentative and subtle differences but require further exploration to robustly assess their use for discrimination purposes. Furthermore, while the older ice-core deposit (GRIP 1734 m; 14 308±177 a BP) is consistent only with the calibrated age range of the BT, the younger deposit (GRIP 1727.75 m/NGRIP 1582.75 m; 14 202±173 a BP) overlaps with the age ranges of both the BT and the PT layers. Although a firm correlation is precluded, we discuss various possibilities below that will require testing in future work.

One possibility is that the GI-1e deposits in the ice represent two closely spaced eruptions that have become ‘fused’ into one BT deposit in some terrestrial records. Indeed, Pyne-O’Donnell et al. (2008) previously alluded to this after observing diffuse BT shard distributions over 10 cm within the cores from Borrobol Bog (green bars, Fig. 7), Loch an t’Suidhe and Tanera Mor (Roberts et al., 1998). A dispersed shard concentration profile is not observed at all sites, however, and a distinct single peak spanning just a few centimetres is observed at Abernethy Forest (Fig. 7) (Matthews et al., 2011). The best age estimate of 14 190–14 003 cal a BP for the BT is derived from the latter site by Bronk Ramsey et al. (2015) and this age range agrees well with the youngest deposit found in the Greenland ice, but also shows some overlap with the upper age range of the older deposit. This is consistent with our

Figure 6. (A–C) Compositional variation diagrams for GS-2.1 rhyolite deposits of NEEM 1524.80 m, GRIP 1818.30 m and NGRIP 1665.60 m against North Iceland Shelf data from cores MD99-2271 (Gudmundsdottir et al., 2011), MD99-2271, MD99-2272 and MD99-2275 (this study). Error bars are 2σ of replicate analyses of the Lipari obsidian secondary standard.

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Shard numbers/0.5 cm

Figure 7. Stratigraphic position of GI-1e tephra deposits. GRIP 1734 m, GRIP 1727.75 m and NGRIP 1582.75 m against δ 18O records and potential BT and PT tie-points in Borrobol and Abernethy Forest cores, Scotland. Loss on ignition (LOI) and shard concentration data are from Pyne-O'Donnell et al. (2008) and Matthews et al. (2011). The chironomid-inferred mean July temperature record from Abernethy Forest is shown to highlight the relative positions of the BT and PT (Brooks, 2012) with ages from Bronk Ramsey et al. (2015). The solid green line represents a scenario where the PT is absent in the Greenland ice and the two GI-1e ice deposits have been fused into a single diffuse layer in the terrestrial record, potentially shown in the wide Borrobol Bog shard profile. The dashed green line represents another possible scenario where any BT deposit found in Lateglacial terrestrial records should be synchronized to both ice-core deposits spanning a 106-year interval. This proposed correlation is consistent with the Scottish chironomid-inferred temperature record from Whitrig Bog that indicates the BT deposition occurred during an interval that equates with the late GI-1e in Greenland (Brooks and Birks, 2000; Walker and Lowe, in press) (Fig. 7). However, what we cannot rule out is that climatic changes between Greenland and Scotland during GI-1 were time-transgressive, meaning that we cannot rely on climatostratigraphic constraints to support our tephra correlations. We assume that the PT is absent in Greenland as we did not identify any tephras of similar composition within GI-1d ice. An alternative scenario, however, is that ash from both the BT and the PT were instead deposited in Greenland during GI-1e, as the older GRIP 1734 m and younger GRIP 1727.75 m/NGRIP 1582.75 m deposit, respectively. We believe that this scenario is unlikely given the implied prolonged delay in climatic response between Greenland and Scotland (Fig. 7). However, we stress the ultimate goal here of employing the BT and PT as independent marker horizons without having to rely on stratigraphic positions to aid and support a correlation. This is a significant challenge given the complexity associated with the BT and PT but some promising signs are presented in relation to the trace element signatures. We urgently need to strive for better geochemical fingerprints to discriminate between the BT and PT so that potential correlations to the ice can be tested.

The tephra identified in GS-2.1 is simpler in terms of its wider application as an ice-marine tie-point. This is the oldest known deposit with a Borrobol-type composition, but we demonstrate that it can be separated from the BT and PT on the basis of CaO vs. TiO2 content (Fig. 3C). This compositional difference will be valuable in poorly resolved marine or terrestrial sediments and should circumvent any potential miscorrelations with BT or PT deposits. Found in all three ice cores with high shard concentrations and dated to 17 326 ± 319 a BP (Table 1; Fig. 2), this tephra has huge potential as a time-synchronous marker horizon for an interval that often poses dating challenges. For the ice, GS-2.1 has few match points between ice cores, and this new interval that often poses dating challenges. For the ice, GS-2.1 has few match points between ice cores, and this new

tentative observation that fractional crystallization of feldspar and zircon links BO521 (i.e. BT) more favourably with GRIP 1727.75 m/NGRIP 1582.75 m than GRIP 1734 m, based on higher concentrations of elements such as Y and Al in the latter.

It is therefore possible that some terrestrial sites preserve the GI-1e tephra couplet as a diffuse unit (e.g. Borrobol Bog), whereas other sites (e.g. Abernethy Forest) may only preserve one of these ice-core deposits (Fig. 7). The ability to temporally resolve closely spaced volcanic events is a strength afforded to high-resolution ice cores and, in this context, creates a need to reinvestigate terrestrial samples in ultra-fine resolution, to explore the finer anatomy of the BT in terrestrial records. This, however, may not be possible due to the relatively lower resolution of terrestrial records. Nevertheless, based on our current data sets, we can suggest that any BT deposit found in Late Glacial terrestrial records should be synchronized to both ice-core deposits spanning a 106-year interval. This proposed correlation is consistent with the Scottish chironomid-inferred temperature record from Whitrig Bog that indicates the BT deposition occurred during an interval that equates with the late GI-1e in Greenland (Brooks and Birks, 2000; Walker and Lowe, in press) (Fig. 7). However, what we cannot rule out is that climatic changes between Greenland and Scotland during GI-1 were time-transgressive, meaning that we cannot rely on climatostratigraphic constraints to support our tephra correlations. We assume that the PT is absent in Greenland as we did not identify any tephras of similar composition within GI-1d ice. An alternative scenario, however, is that ash from both the BT and the PT were instead deposited in Greenland during GI-1e, as the older GRIP 1734 m and younger GRIP 1727.75 m/NGRIP 1582.75 m deposit, respectively. We believe that this scenario is unlikely given the implied prolonged delay in climatic response between Greenland and Scotland (Fig. 7). However, we stress the ultimate goal here of employing the BT and PT as independent marker horizons without having to rely on stratigraphic positions to aid and support a correlation. This is a significant challenge given the complexity associated with the BT and PT but some promising signs are presented in relation to the trace element signatures. We urgently need to strive for better geochemical fingerprints to discriminate between the BT and PT so that potential correlations to the ice can be tested.

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name for this deposit – GS-2.1-RHY – based on its position in the Greenland stratigraphic framework and its geochemical composition.

Conclusions

Adopting a contiguous ice-core sampling approach has provided further insight into the complexity of the Borrolool Tephra. Two cryptotephra deposits detected in GI-1e ice probably equate to the BT found in terrestrial records but a firm correlation is precluded given the indistinguishable composition and closely timed deposition of the BT and PT. In this study trace element compositions show possible but tentative signs that may prove fruitful for future discrimination purposes. If these deposits are to be used as valuable marker deposits, further work is urgently required in this area. As yet there are no trace element analyses from terrestrial records that contain both the PT and the BT, and this is essential if differences are to be observed between these deposits. Re-analysis of BT and PT major element signatures with improved microprobe operating conditions may also prove beneficial to tease out any subtle differences that may be obscured by analytical noise. Furthermore, ultra-high-resolution sampling of Scottish Lateglacial sequences together with high-precision chronologies may prove beneficial to unpick the diffuse tephra profiles associated with the BT. Lastly, the GS-2.1-RHY horizon identified in three ice cores illustrates the value of marine-ice tie-points in an interval plagued by dating uncertainties and highlights its potential to assess marine reservoir offsets for the North Iceland Shelf.

Supporting information

Supporting information relating to this article can be accessed via the publisher’s website.

Table S1. Major oxide concentrations and secondary standards.

Table S2. Trace element data.

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Abbreviations. AMS, accelerated mass spectrometry; CFA, continuous flow analysis; EPMA, electron probe micro-analysis; GI, Greenland intercalibration; LA-ICP-MS, laser ablation inductively-coupled plasma mass spectrometry; MCE, maximum counting error; NA, North Atlantic; REE, rare earth element; SC, similarity coefficient; TA, total alkalai; TAU, tephra analysis unit; WD, wavelength dispersive; WDS, wavelength dispersive spectrometry; XRF, X-ray fluorescence.

References

Boone AJ, Cook E, Abbott PM et al. 2015. A tephra lattice for Greenland and a reconstruction of volcanic events spanning 25–45 ka b2k. Quaternary Science Reviews 118: 122–141.
Brøk RAMS C, Abbott PG, Blokkey SP et al. 2015. Improved age estimates for key Late Quaternary European tephra horizons in the RESET lattice. Quaternary Science Reviews 118: 18–32.


Jarvis RJV. 2013. Palaeoceanographic and climatic changes during the Late Weichselian and the Holocene off North Iceland: foraminifera and stable isotopes. MSc Thesis, University of Aarhus.


Rasmussen SO, Bigler M, Blockley SP et al. 2014. A stratigraphic framework for abrupt climatic changes during the Last Glacial period based on three synchronized Greenland ice-core records.
refining and extending the INTIMATE event stratigraphy. Quaternary Science Reviews 106: 14–28.
Seierstad IK, Abbott PM, Bigler M et al. 2014. Consistently dated records from the Greenland GRIP, GISP2 and NGRIP ice cores for the past 104 ka reveal regional millennial-scale δ¹⁸O gradients with possible Heinrich event imprint. Quaternary Science Reviews 106: 29–46.