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Article

Accepted Version

MacLeod, A. and Davies, S. M. (2016) Caution in cryptotephra correlation: resolving Lateglacial chemical controversies at Sluggan Bog, Northern Ireland. Journal of Quaternary Science, 31 (4). pp. 406-415. ISSN 0267-8179 doi: 10.1002/jqs.2858 Available at https://centaur.reading.ac.uk/77197/

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Published version at: http://dx.doi.org/10.1002/jqs.2858
To link to this article DOI: http://dx.doi.org/10.1002/jqs.2858

Publisher: Wiley

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Caution in cryptotephra correlation: resolving Late-glacial chemical controversies at Sluggan Bog, Northern Ireland.

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Abstract

Tephra layers are valuable stratigraphic and chronological markers in palaeoenviromental studies. Establishing robust linkages require complete comparative databases of eruptive events to ensure that potential correlatives are not overlooked. This is achieved through the construction of tephrostratigraphical inventories proximal to the volcanic source. Proximally-characterised ash layers are frequently detected thousands of kilometres from source alongside limited numbers of tephras with no apparent proximal correlative. Despite the inability to correlate to a specific eruption, source volcanoes can be proposed and many of these far-field occurrences have become well-established stratigraphic markers. However, careful scrutiny is essential to verify the primary and instantaneous fallout origin of these distant occurrences. Here we present new data which proposes explanation for the long-standing controversy surrounding the source of Late-glacial age cryptotephras within Sluggan Bog, Northern Ireland. Chemical analysis of glass shards detected within this sequence are proposed to originate from an obsidian exposure located 11 km from the site, rather than from a contemporaneous eruptive event. This discovery highlights the importance of giving appropriate consideration to the enclosing geology of a particular palaeorecord. We suggest locations where geological sources might complicate air-fall records of tephra deposition and propose a means by which to address this challenge.

Key Words: Tephra, Sandy Braes Obsidian, Sluggan Bog, Late-glacial Interstadial

Introduction

Establishing the sequence and chemical composition of eruptive events is a crucial first-step in the successful application of tephrochronology (Lowe, 2011; Davies, 2015). A synthesis of eruptive ages and chemical fingerprints, primarily established from proximal deposits, allow correlations to be determined and isochrons to be drawn (e.g. Thórarinsson, 1981, Kvamme *et al.,* 1989, Björck *et al.,* 1992, Haflidason et al

2000; Larsen and Eiríksson, 2008). In recent years, these frameworks have been expanded with discoveries of new cryptotephra deposits in areas that are far removed from the volcanic centres and seem to have no apparent proximal correlative (e.g. Turney *et al.,* 2006, Lowe, *et al.,* 2008; Blockley *et al.,* 2014, Lawson *et al.,* 2012). Prior to correlation, each new cryptotephra find requires a thorough assessment of its primary nature. In areas such as Iceland, where the proximal records are truncated due to glaciation, volcanic sources can, in most cases, be proposed based on the compositional data outlined in a number of databases (e.g. Tephrabase : Newton *et al.,* 2007 and RESET: Bronk Ramsey *et al.,* 2015). Establishing a source, however, is not easy, especially in cases where the distal compositional data-set is based on the analysis of a limited number of glass shards (e.g. Wastegård *et al.,* 2003, Pilcher *et al.,* 2005, Abbott and Davies, 2012, Lind *et al.,* 2013, Jouannic *et al.,* 2014). The focus of this paper is on the uncorrelated Late-glacial deposits within the Sluggan Bog sequence originally identified as tephras (Turney et al., 2006; Lowe et al., 2008). These 'tephras' represent single-site occurrences of unknown source, yet were flagged as potential isochrons for the Late-glacial period.

Sluggan Bog in Co. Antrim has been the focus of in-depth chronological and palaeoecological investigation for more than 20 years. Much of the early research (Pilcher and Hall, 1992; Hall *et al.,* 1993; Pilcher *et al.,* 1995; Plunkett, 2006) concentrated primarily on the sediments of Mid-Late Holocene age, whereas Lowe *et al.* (2004) and Turney *et al.* (2006) provide more in-depth analysis of sediments accumulated during the last glacial-interglacial transition (LGIT, 16,000 – 8000 a BP). A minimum of seven discrete volcanic ash layers have been identified within this sequence, all of which have been chemically characterised and which, from radiocarbon and age-modelling techniques, span the period from about 14,500 cal a BP (Turney *et al.,* 2006) to AD 1510 (Hall *et al.,* 1993; Pilcher *et al.,* 1995; Plunkett, 2006).

The Holocene ash layers have, in most cases, been correlated with well-documented and chemically characterised Icelandic eruptions. However, the origins of those from the Late-glacial period remain equivocal. Davies (2003) and Lowe *et al.* (2004) report three prominent and several more minor peaks in glass concentration over this time period (Figure 1). They proposed tentative correlations based on the stratigraphic positions and ^{14}C ages of prominent North Atlantic isochrons known at that time. As such, they suggested that these ash layers could represent occurrences of the mid-Nahanagan Stadial Icelandic Vedde Ash (12,235 – 12,007 cal a BP; Rasmussen *et al.,* 2006), the late Woodgrange Interstadial Laacher See tephra (12,920 – 12,840 cal a BP; Brauer *et al.,* 1999) from the Eifel region and the early Woodgrange Interstadial Icelandic Borrobol tephra (14,190 – 14,003 cal a BP; Bronk Ramsey et al. 2015) (Figure 1). However, compositional data obtained on the oldest and youngest of the

layers, at 56 cm OD (Sluggan A) and 16 cm OD respectively, revealed chemical signatures that were inconsistent with any known eruption from the time period. No data was obtained from the layer at 25 cm (Sluggan B). Lowe et al. (2004) suggested that these may therefore represent new and previously uncharacterised ash deposits or alternatively be a consequence of chemical alteration of known tephras in this particular depositional environment or during sample processing and analysis. Here we present new compositional data and a revised model for volcanic glass deposition at Sluggan Bog during the Late-glacial.

Site location and Quaternary context

Sluggan Bog is a raised bog located approximately 3 km northeast of Randalstown in Co. Antrim, Northern Ireland (N 54.779568°, W -6.300798°; Figure 2). Lowe *et al.* (2004) describe the sediment stratigraphy from an open section at Sluggan Bog as matrix supported diamict overlain by horizontally-bedded, macrofossil-rich organic sediments possibly deposited within a shallow, stagnant water body. This latter unit is then succeeded by silty clay and finally by peats, the upper portion of which has been exploited for fuel. An age-depth model has been constructed from a series of 75 radiocarbon dates (Lowe *et al.,* 2004). This places the base of the sequence at between 14,500 – 14,000 cal a BP and, in combination with other palaeoecological proxies (Smith and Goddard, 1991), suggest the site records the palaeoenvironmental response to climatic change from the Woodgrange Interstadial, through the Nahanagan Stadial and into the Holocene. During the last glacial period, it is considered that this region of Northern Ireland was inundated by ice advancing south from the Scottish Mainland and also by ice caps emanating from the Antrim Hills to the East and Sperrin Mountains to the West (Charlesworth, 1938; Greenwood and Clark, 2009). From these studies it is thought that the region around Sluggan Bog would have become ice-free sometime after 16,000 ka BP.

Local geology

The bedrock geology in the region is dominated by Lower Tertiary (c. 61 Ma; Ganerød et al., 2014) basalt lava flows, however there are restricted exposures of rhyolitic and obsidian tuffs and agglomerates. Meighan (1981; 1984) reports occurrences of these in the vicinity of Tardree Mountain (N 54.796627°, W -6.1253907°, Sandy Braes) and in two locations to the north of Ballymena (N 54.908747°, W -6.279238° (Kirkinriola) and N 54.908747°, W -6.235082° (Quarrytown)). The first of these, the Sandy Braes, outcrops approximately 11 km East of Sluggan Bog, whereas Kirkinriola and Quarrytown are located approximately 15km to the North (Meighan, 1981). The Sandy Braes site is the only one of these known to produce glass of acid rhyolite composition. Obsidian, perlite and pitchstone such as is found at Sandy Braes, is a product of rapid cooling following extrusion of igneous material at the earth's surface. This rapid

cooling produces a rock resembling a frozen liquid or glass rather than developing a crystal form. Perlite and pitchstone is a form of obsidian which has undergone post-depositional modification by hydration.

Methods

The intention of this research was not to repeat the work of Davies (2003) and Lowe *et al.,* (2004) but instead to test the reproducibility of their EPMA data and attempt to finally pinpoint potential correlatives. This was in response to concerns by Lowe et al. (2004) that chemical treatment applied during sample preparation may have affected their final shard chemical compositions. In order to test this, a sample from 56 cm (the largest peak) was re-prepared from the Sluggan Bog sequence solely using the density separation procedure reported by Turney (1998) and Blockley *et al.* (2005). This omits the use of heat or strong acids which are thought to alter the original chemical composition of the tephra shards, although there may be some specific instances where this effect is more restricted (Dugmore *et al.,* 1995; Blockley *et al.,* 2005; Roland *et al.,* 2015). Individual grains were handpicked onto resin stubs, sectioned and polished before being analysed on a Wavelength Dispersive Electron Microprobe (WDS-EPMA) at the Tephra Analytical Unit within Edinburgh University. The original work by Davies (2003) utilised both the Edinburgh and Belfast electron microprobe facilities and details of all operating conditions are included in supplementary table ST1. A cut-off of 95% (two decimal places) was applied to analytical totals when filtering the data (Hunt and Hill, 1993). In addition to the sample at 56 cm, two control samples were taken from the sequence to test for the persistent presence of SBO chemistry and to compare with the previously analysed layers. The first was obtained from a level where no tephra had previously been detected (46-51 cm), while the second was taken from within a zone of low tephra shard counts (30-35 cm). These were also prepared using the Turney et al. (1998) technique.

Due to the volcanic nature of the local bedrock and the nearby presence of an obsidian outcrop, a sample of Sandy Braes Obsidian (SBO) was obtained from the Geological Survey of Northern Ireland (Figure 3). A representative portion of the glassy component (avoiding quartz and feldspar porphyries) was ground using a pestle and mortar and sieved, to isolate the same fraction as in Sluggan Bog, before being mounted on a resin stub. All tephra and obsidian samples were analysed for 13 major and minor element oxides on a Cameca SX-100 electron microprobe fitted with five spectrometers and calibrated using internationally recognised primary and secondary standard blocks (Hunt and Hill, 1996; Jochum et al. 2005). Microprobe operating conditions are summarised in supplementary table ST1.

Results

Tephrostratigraphy

Sluggan Bog 56cm (A), 25cm (B), 16cm.

The shard concentration peak at 56 cm depth (Sluggan A, Turney *et al.,* 2006) is the largest identified by Lowe *et al.* (2004) and its occurrence coincides with the transition from a matrix-supported diamict to overlying organic units, the latter radiocarbon dated to the early part of the Woodgrange Interstadial (15,004 – 14,159 cal a BP; recalibrated from Walker *et al.* 2012 using the IntCal13 calibration curve; Reimer *et al.,* 2013). Approximately 65 colourless shards cm^{-3} (Figure 1) were detected at this level declining to less than 10 shards in the overlying 5 cm. The size of the grains extracted from the monolith are in the 80-25 micron range which is considered to comprise the predominant size distribution of atmospherically-transported distal ash across Northern Europe (Mangerud *et al.,* 1984), however some variation in this can be observed (Stevenson et al., 2012). Although the chemical data were not reported in Lowe et al. (2004), seven glass shards were analysed by WDS-EPMA and these are of a consistent rhyolitic composition (Figure 4; Davies, 2003). Twenty-five glass shards were analysed from the deposit at 16 cm depth (17 and eight shards analysed on the Edinburgh and Belfast microprobes respectively; Davies, 2003). The data from both deposits highlight their similar chemical compositions (Figure 4 and supplementary Table ST2). The deposit at 16 cm shows coherence with the layer at 56cm, however the data are not as tightly clustered. Fifteen further WDS-EPMA data points were obtained for this study from 56 cm depth in 2011. These reveal a similar rhyolite classification and, from Figure 4, suggest an indistinguishable composition from that outlined in the original work.

Lowe et al. (2004) outline the identification of a third tephra deposit at 25 cm depth in the sequence (referred to as Sluggan B by Turney et al., 2006). Despite several attempts, no shards were recovered for analysis by electron microprobe in the current or previous study (Davies, 2003). This may be due to variations in shard concentrations across the monolith samples. Without any supporting geochemical information, however, we cannot validate its identity as a tephra deposit.

Sluggan Bog 46-51cm

No tephra was previously reported from this part of the sequence (Figure 1), however on this occasion a very low background of colourless grains typical of volcanic glass shards were detected. Three glass shards from this interval were analysed by WDS-EPMA (see supplementary Table ST2 for data). The chemical composition of the shards is consistent with a rhyolitic source and this profile corresponds well with the grains identified from the sample at 56 cm. The occurrence of these very low shard concentrations may reflect an upward mixing of particles which was not detected in the original investigation due to within core variations in shard concentrations.

Sluggan Bog 30-35cm

In the original work, this section of the core was identified to contain a dispersed zone of colourless tephra shards which extends from 30-40 cm below OD. No chemical data had previously been obtained from this level. However, because of its stratigraphic position within the Woodgrange Interstadial, and the questions raised over the chemistry of the other layers in the sequence, it was considered important to assess its chemical signature. Only one data point was obtained due to the very low shard concentrations present and therefore it is impossible to say whether this is representative of the entire 10 cm interval (see supplementary Table ST2 for data). With this limited information, the chemistry of this shard is most similar to published data from either the Borrobol or Penifiler tephras (Figure 4), however the most precise age estimate we have for this section of the sequence, c.13,650-13,125 cal a BP (Lowe *et al.,* 2004; Walker *et al.,* 2012) would mean that this tephra is younger, by at least 150 years, than the youngest proposed age of the Penifiler tephra (14,063-13,808 cal a BP; Bronk Ramsey *et al.,* 2015). It could therefore represent reworking of very small quantities of the Penifiler tephra, an ash layer frequently identified across the British Isles (Pyne-O'Donnell 2007). However, as this tephra deposit has not yet been identified in Ireland, potential sources for this reworked material remain to be found. Consequently, its occurrence is considered to be of no stratigraphic/chronological significance in this instance. This demonstrates the advantage of considering combined dating strategies to identify potential issues such as this.

Sandy Braes Porphyritic Obsidian and comparison to Sluggan tephras

As a hand specimen, the SBO (Figure 3a) is highly friable and contains abundant (c.25%) quartz and feldspathic (sanidine) phenocrysts (Meighan, 1981; Ganerød *et al.,* 2011) held within a dark matrix of glassy lustre. When crushed, mounted in Canada Balsam and examined under plane polarised light, the glass component appears brown in colour, ranging from very pale to dark hues (Figure 3b). Conversely, at Sluggan Bog, this study and Davies (2003) note that the shards from 56 cm and 16 cm are platy, colourless and appear weathered with jagged edges, pitted surfaces and some spherical vesicles (Figure 3e-f). With the exception of the platy morphology, the visual characteristics of the Sandy Braes Obsidian (Figure 3) are quite different from those at Sluggan Bog. However, it is possible that the particles assigned to the Sluggan 56 and 16 cm tephra layers have been altered in their depositional environment, either while exposed at the surface or within the acid organic-rich host sediments (Pollard et al. 2003). This may have resulted in leaching of the elements from an originally brown-coloured particle leaving behind a platy colourless shard which over time has become pitted on the surface in response to the acidic conditions.

Pollard *et al.* (2003) and Dugmore *et al.* (1992) demonstrate that silicic, and particularly rhyolitic, ash layers appear to be chemically very stable in the depositional environment over several thousands of years. Blockley et al. (2005), however suggest that when shards are immersed in moderate to highly acidic or basic environments for several hours that chemical modification of the leachate takes place, along with significant pitting and corrosion of the shard surfaces. The depth to which this alteration has penetrated within the shard is unknown. Dugmore et al. (1992) also highlight the visible effects of weathering on shard degradation when exposed within a soil profile on Iceland.

Prior to chemical analysis, SBO grains were mounted in the same way as those from Sluggan Bog and the final preparation produced a polished surface very similar to those from explosive volcanic material (Figure 3c and d). Fifteen grains were analysed by WDS-EPMA from this sample. Due to the presence of quartz and feldspar mineral inclusions in the glass, backscatter electron imaging was used to ensure only homogeneous glass targets were analysed.

The chemical data from all three deposits analysed (SBO, Sluggan Bog 56 and 16 cm) are tightly clustered revealing a rhyolitic classification (Figure 4 and supplementary table ST2). When compared to published Icelandic data of a similar classification an offset is apparent relating to higher total alkali values in the SBO and Sluggan Bog samples and this is particularly noticeable in the K_2O data. Davies (2003) noted difficulty in identifying any European volcanic source region with alkali values such as those identified at 56 and 16 cm depth, whereas Figure 4 demonstrates a clear overlap with the SBO data. Bi-variate plots of other major element oxides (Fe, Mg and Ca) also support this offset (Supplementary Figure SF1) and highlights a chemical overlap between the Sluggan 'tephra' deposits and the SBO. Consequently we propose this geological outcrop as the source and as such no chronological significance should be placed on these deposits. Also included in Figure 4 are XRF data for the SBO from Patterson (1952), Cameron and Sabine (1969) and EPMA data from Brooks *et al.,* (1981). It should be noted that XRF analysis is not a directly comparable analytical technique to EPMA, however the majority of analyses demonstrate, by independent means, some affinity with the glass data presented here. The data from Patterson (1952) is an outlier and may reflect greater heterogeneity than has been captured by our data. Further examination of the compositional data from the SBO, suggests that the brown colouration is not bound into the glass network as iron because the oxide concentrations are only in the order of 1.5 – 2 weight % and this may explain why it is able to be removed from the grains. Although no chemical data has been obtained from the layer at 25 cm depth (Sluggan B, Turney *et al.,* 2006), it is also possible that this deposit may be derived from the same origin as those at 56 and 16 cm and should also not be considered as an isochron.

Mechanism for occurrence in Sluggan Bog

We propose a mechanism for the preservation of volcanic glass shards within the Woodgrange Interstadial and Nahanagan Stadial sediments at Sluggan Bog. During the initial phase of glaciation in Northern Ireland at c. 35 ka BP, Scottish ice is thought to have advanced across the region from the north and east (Greenwood and Clark, 2009). Ice masses developed in the hills to the north and west of Sluggan Bog and when these ice masses coalesced with Scottish ice, more complex ice-flow patterns developed (Greenwood and Clark, 2009). The diamictic units, preserved at the base of the Sluggan Bog sequence, (Figure 1) are likely to be the product of these different phases of Scottish mainland and local ice. Located only 11 km from Sluggan Bog, it is proposed that the SBO was overridden by ice resulting in crushing and transportation of this very friable material and then subsequent incorporation into the till or outwash deposits as ice advanced or receded across the region. This material was then left exposed on the land surface to be weathered, remobilised and finally incorporated, perhaps by aeolian processes, into the peat which grew during the Woodgrange Interstadial. Similarly, it is proposed that remobilisation of previously deposited sediment, as a result of enhanced fluvial and periglacial activity during the Nahanagan Stadial, allowed incorporation of the SBO within these sediments. The dispersed zone of glass particles observed during the Nahanagan Stadial suggests the persistence of this material in the surrounding landscape (Figure 1). Further analysis is needed to determine whether the influx and concentration of grains into Sluggan Bog occurred during periods of landscape instability and to explain the apparent disparity in morphological characteristics between the SBO outcrop and the Sluggan Bog grains. There is no clear indication that grains originating from the SBO were deposited during the Holocene at Sluggan Bog. Pilcher *et al.* (1995) report a single shard analysis which stands out from those relating to the AD860 layer in Sluggan Bog (Wastegård et al., 2003) and which has alkali values consistent with the SBO. However, the other elements and other analyses from this analysis do not correspond as closely.

Our findings highlight a potential issue associated with stratigraphic and chronological correlations which utilise cryptotephra deposits. In this specific case, we acknowledge that the implications of this may be restricted to studies in this part of Northern Ireland, due to the relatively small size of the SBO outcrop and restricted distribution potential of the material. However the principle of the process has wider applicability to tephrochronologists working in regions where outcrops of this kind are more prevalent, both in the UK and further afield.

Tertiary volcanics are prevalent along the length of the west coast of Scotland from Arran in the south to the Isle of Skye in the north. These regions, like Sluggan Bog, have been subjected to multiple phases of glacial erosion and weathering. Thorpe and Thorpe (1984) report the presence and composition of the glassy, obsidian-like pitchstone at each of the locations highlighted in Figure 5. During the LGM the dominant ice flow pathway from the Scottish sources is off shore to the west. However, during the Loch Lomond Stadial, radial ice flow in the high land in the vicinity of these outcrops could result in incorporation within lake and bog sequences. When the

Scottish obsidian data are compared to that of published Late-glacial tephra compositional data from nearby sequences spanning the appropriate time period as indicated by the Lowe et al. (2004) ^{14}C chronology, some striking similarities emerge. Bivariate chemical plots of these data from Thorpe and Thorpe (1984) show clear affinity of the Arran Corrygills (AP4) and Arran Tormore (AP1) outcrops to what are considered to be well-characterised deposits of Borrobol-type tephra chemistry (Figure 6). Other outcrops display similarities to products of other Icelandic volcanic centres, particularly Askja and Hekla. Further work is required to analyse these obsidian/pitchstone sources, with the same analytical techniques as employed for tephra work, in order to develop a robust database of tephra mimics which are of no chronological significance. Ash layers of Borrobol-type chemistry are recorded in widely separated localities from Iceland (off-shore; Eiríksson et al., 2000) and Scandinavia (Davies et al., 2003; Wastegård, 2005), thousands of kilometres from the Scottish obsidian sources and in regions where obsidian and pitchstone have not been reported. As such, it is clear that a primary air-fall eruptive event has occurred during the early Late-glacial interstadial, most likely originating from Iceland (Davies et al., 2003). However, if grains with similar chemistry are identified in regions in close proximity to obsidian exposures and in stratigraphic positions incompatible with the regional tephrostratigraphical framework, caution in interpretation is advised.

Conclusions

1. Late-glacial 'tephra' deposits at Sluggan Bog are thought to be secondary products sourced from nearby igneous outcrops. These deposits have been incorporated into published tephrostratigraphic schemes for the Late-glacial, however they are events derived from catchment processes rather than primary air-fall and as such no chronological significance should be placed on their occurrence.
2. These results highlight the importance of assessing and eliminating local geological sources prior to finalising correlations and particularly before proposing new, previously unrecognised ash layers where source regions are uncertain. We recommend that each new cryptotephra discovery should be assessed to ensure, as far as is possible, that it reflects a primary deposit and is the product of a contemporaneous volcanic eruption.
3. While this case study is directly applicable to tephrochronologists working in the UK, it also has implications for those working in regions around the world where vitreous igneous outcrops have the potential to be mobilised in a range of depositional and climatic settings.
4. Incorporation of this type of material into lacustrine and mire contexts might be expected to be more frequent around abrupt stratigraphic and environmental transitions when destabilisation of the landscape takes place, as has been observed at Sluggan Bog.

5. If source regions are well-characterised, it may be possible to utilise obsidian, pitchstone and perlite occurrences as erratic indicators of former ice-flow pathways.
6. Where chemical matches are observed between air-fall tephra deposits and geological sources, detailed analysis of grain-size profiles may assist in unravelling questions regarding primary or secondary deposition, however this will depend on the processes operating to incorporate the grains into sequences.

Acknowledgements

Thanks are extended to Mark Cooper of the Geological Survey of Northern Ireland (GSNI) for supplying a sample of Sandy Braes Obsidian, to Peter Hill (deceased), and Christopher Hayward of the Tephra Analytical Unit at Edinburgh University for their assistance with WDS-EPMA analysis and to Jenny Kynaston (RHUL) for her assistance with the figures. Much of this work was carried out while SMD was in receipt of a NERC PhD studentship (GT04/99/ES/162) and was completed while AM was in receipt of a Leverhulme Trust Early Career Fellowship (ECF-2013-505). SMD is also supported by the ERC (Starting grant TRACE: 259253) and Leverhulme Trust (Philip Leverhulme prize). This article is RHOXTOR publication number RHOX/046. We also acknowledge the considerable volume of work that has previously been conducted on Sluggan Bog by John Lowe, Chris Turney, Mike Walker and their associated colleagues and students. Two anonymous reviewers are thanked for their comments which have improved this final manuscript.

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Figure captions

Figure 1. Sluggan Bog monolith stratigraphy, loss-on-ignition profile and tephra shard count profile modified from Lowe et al. (2004). Davies (2003) obtained WDS-EPMA data on the layers at 16 and 56 cm and the layers 30-35, 46-51 and 56 cm were analysed in this study. No data has been obtained from the layer at 25 cm depth.

Figure 2. Location of Sluggan Bog in Northern Ireland in relation to the obsidian outcrops in the region. This figure has been adapted from Lowe et al. (2004).

Figure 3. A. Hand specimen of the Sandy Braes Obsidian (SBO) showing light-coloured quartz and feldspar held in a glassy, rhyolitic matrix. B. Plane polarised light microscope image of the glass fraction of the SBO following crushing and mounting

in Canada Balsam. C. Grains of SBO in thin section and polished prior to WDS-EPMA analysis. D. Backscatter electron image of a glass shard illustrating a homogeneous surface free of mineral inclusions. E-G. Illustrate the shard-like qualities of the grains detected at 16 and 56 cm in Sluggan Bog. As described in Davies (2003) particles exhibit platy to blocky morphologies, a glassy surface, cuspate edges and open and closed vesicles.

Figure 4. Bivariate plots of published and unpublished WDS-EPMA and XRF data from tephra layers and obsidian outcrops. A) Total Alkali Silica (data normalised to total values) (TAS) biplot illustrating the classification of each of the tephras included in the comparison. Note the inset box containing the data being investigated. B) Expanded TAS plot of the box in A showing the offset in chemistry between the published Borrobol and Penifiler data (RESET database, Bronk Ramsey et al., 2015) and the data from Sluggan Bog (this study) and SBO (this study; data normalised to total values). C) and D) Further bivariate plots illustrating the correlation between the data from this study and Davies (2003) and the SBO (this study; non-normalised). This demonstrates the coherence of the 56 cm and 16 cm deposits with the SBO.

Figure 5. A) Last Glacial Maximum and Loch Lomond Readvance ice limits in the northern half of the British Isles, taken from Chiverrell and Thomas (2010) and including broad ice-flow patterns. Circles highlight the locations of pitchstone/obsidian outcrops identified by Thorpe and Thorpe (1984). Abbreviations of place names are as follows: A: Arran, M: Mull, Ar: Ardnamurchan, E: Eigg, R: Raasay, S: Sluggan.

Figure 6. Bivariate plots illustrating the chemical similarity of the British pitchstone sources to volcanic centres in Iceland and specific Late-glacial tephra deposits identified in the UK. All data from the British pitchstone sites were obtained from Thorpe and Thorpe (1984) and the chemical fields drawn for Askja and Hekla volcanic centres are based on data extracted from the RESET database (Bronk Ramsey et al., 2015).

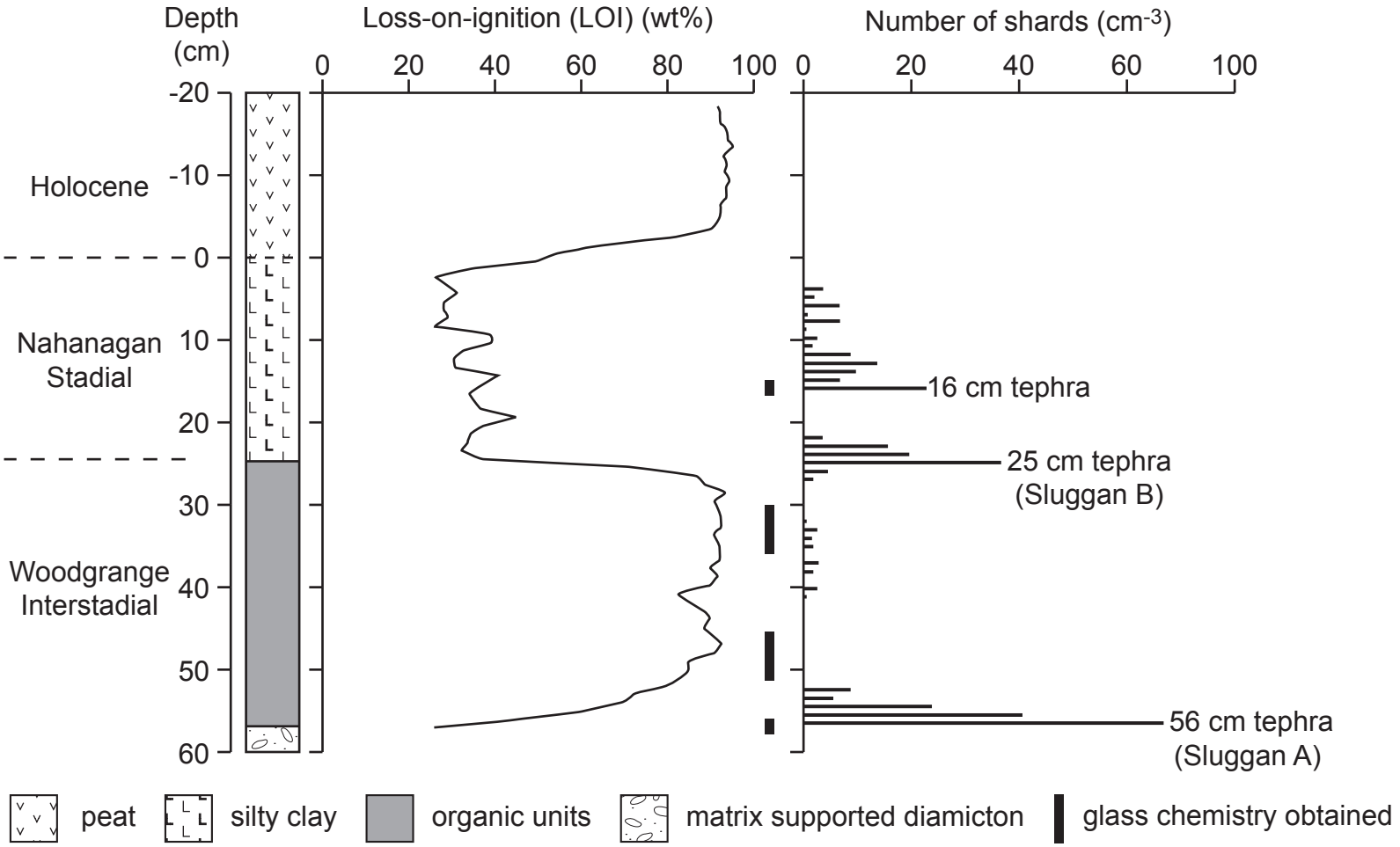
Supplementary table captions

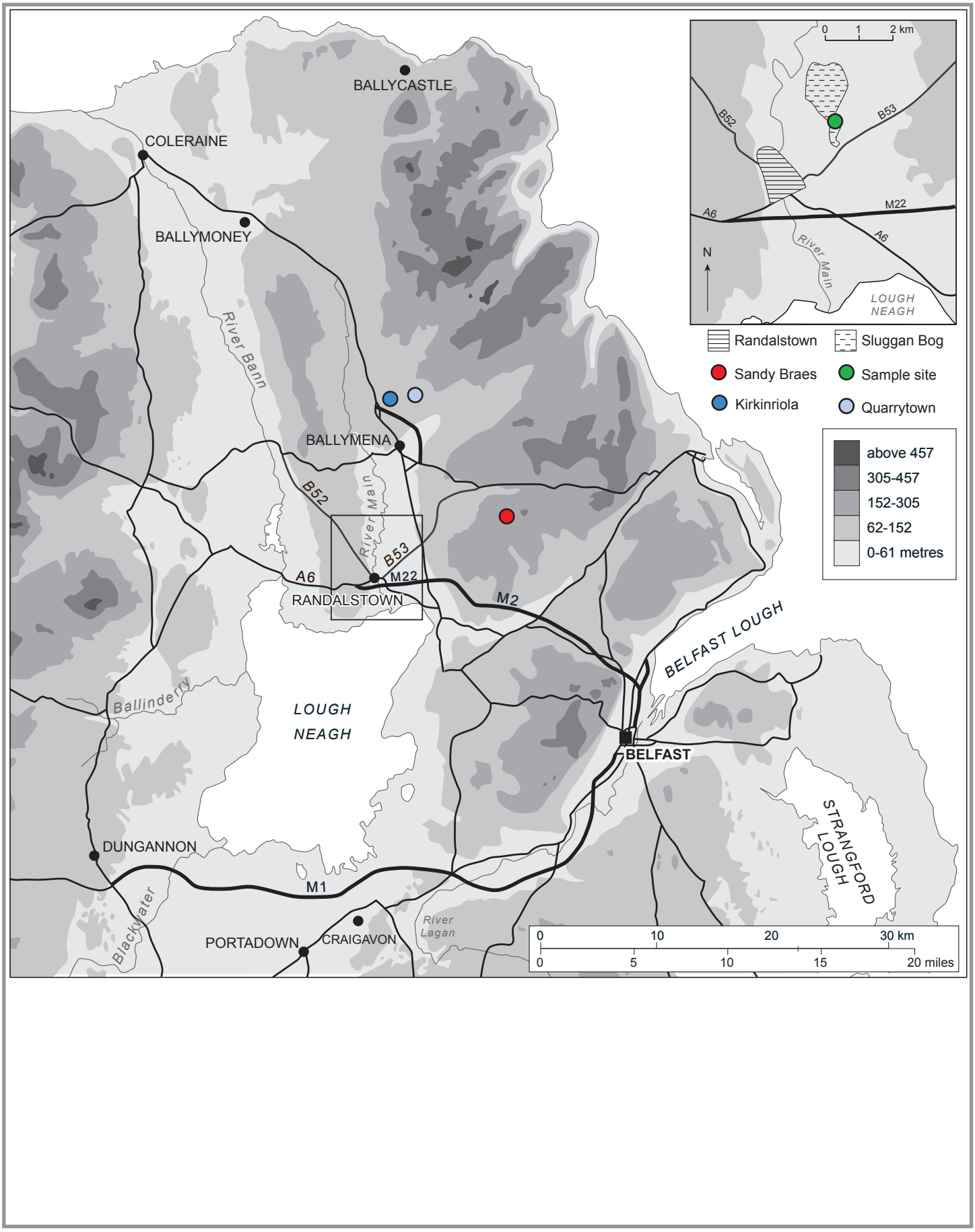
ST1. WDS-EPMA Operating conditions for the CAMECA SX-100 (Tephra Analytical Unit, University of Edinburgh) and JEOL 733 Superprobe (Electron Microscope Unit, Queen's University, Belfast).

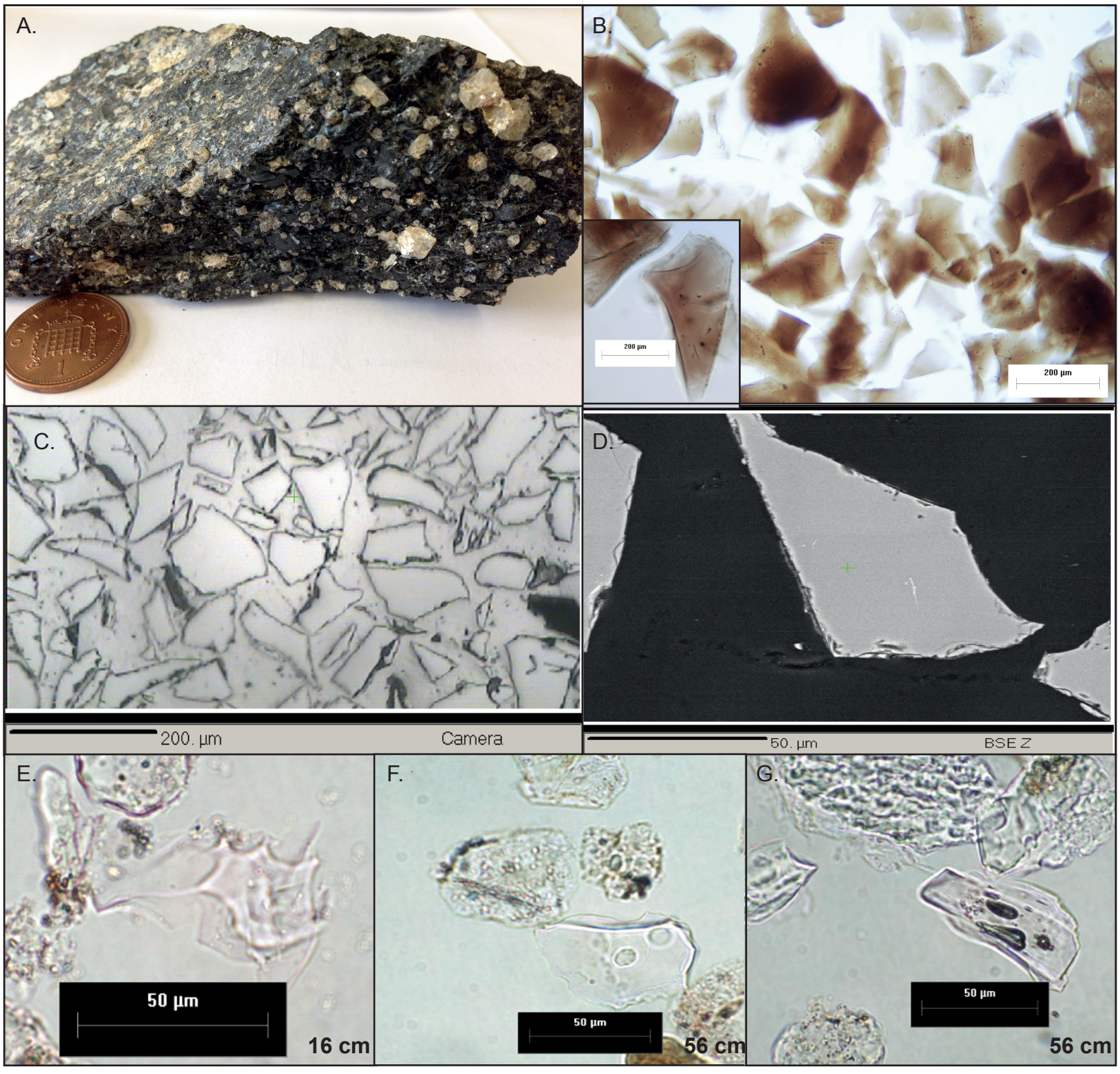
ST2: Major element data measured as oxide concentrations (weight %) via WDS-EPMA for Sluggan Bog tephra layers and Sandy Braes Obsidian. Data lines highlighted in italics have not been included in the final bi-plots as their analytical total values fall below the stated cut-off of 95% (rounded).

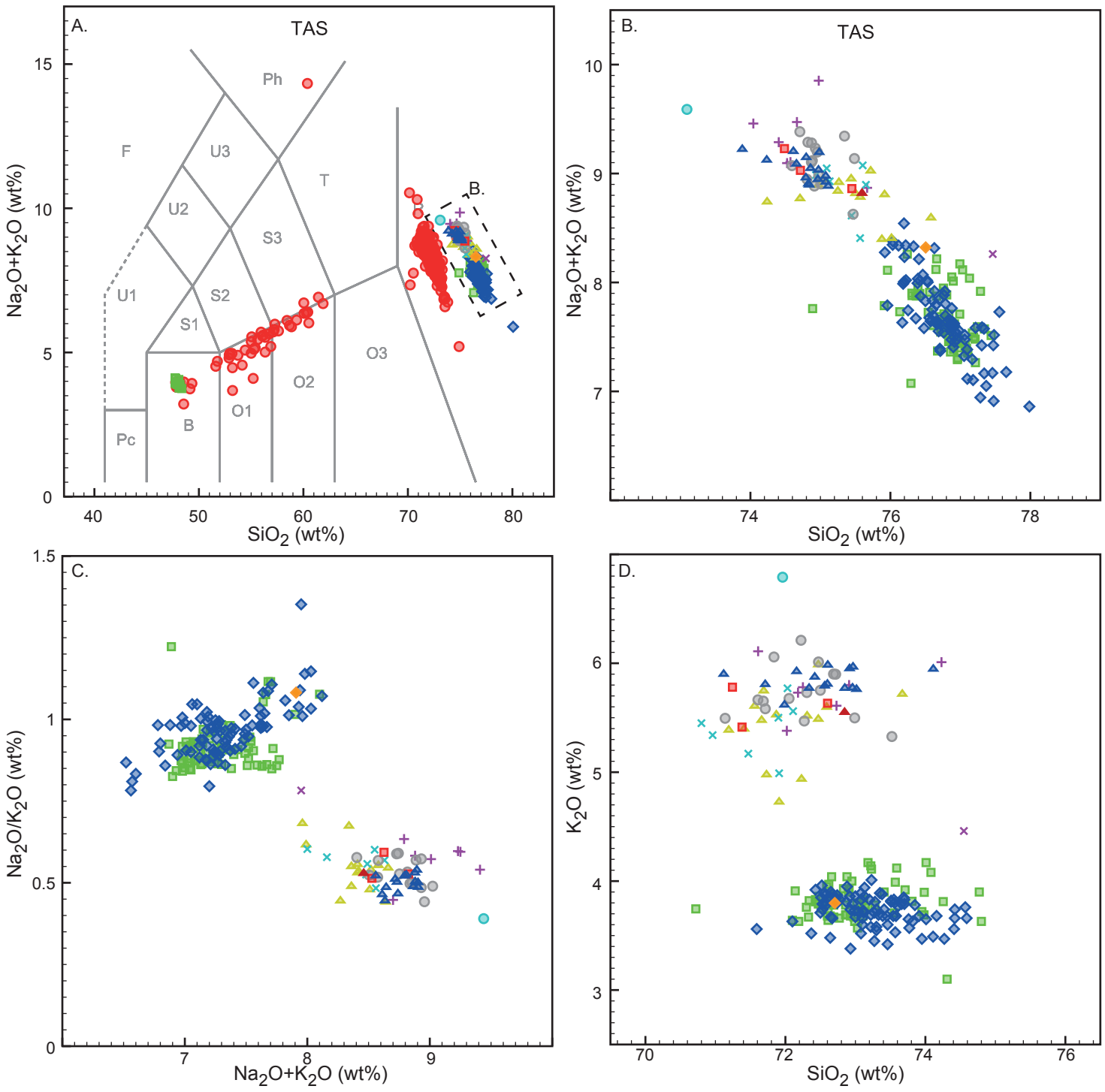
Supplementary figure captions

SF1: Additional bivariate plots of the WDS-EPMA data obtained illustrating the coherence of the Sluggan Bog tephra layers with the SBO and Scottish pitchstone outcrops.

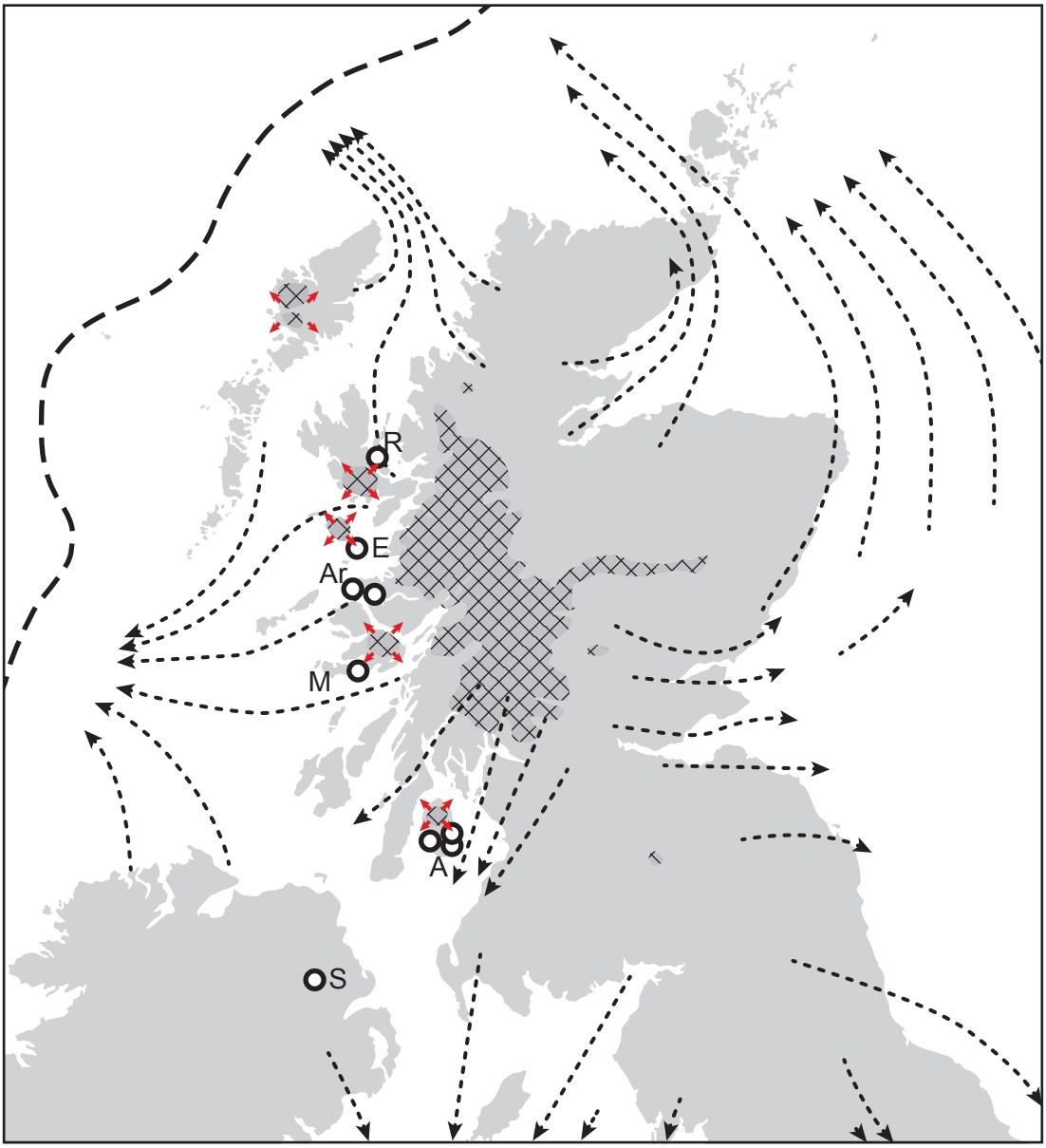

Depth (cm)
Loss-on-ignition (LOI) (wt%)
Number of shards (cm-3)
0
20
40
60
80
100
-20
-10
0
10
20
30
40
50
60
Holocene
Nahanagan Stadial
Woodgrange Interstadial
16 cm tephra
25 cm tephra (Sluggan B)
56 cm tephra (Sluggan A)
peat
silty clay
organic units
matrix supported diamicton
glass chemistry obtained


BALLYCASTLE
COLERAINE
BALLYMONEY
River Bann
BALLYMENA
B52
River Main
B53
A6
M22
RANDALSTOWN
M2
BELFAST LOUGH
Ballinderry
LOUGH
NEAGH
BELFAST
STRANGFORD
LOUGH
DUNGANNON
M1
Blackwater
River
Lagan
PORTADOWN
CRAIGAVON
0 1 2 km
B52
B53
A6
M22
A6
N
River Main
LOUGH
NEAGH
Randalstown
Sluggan Bog
Sandy Braes
Sample site
Kirkinriola
Quarrytown
above 457
305-457
152-305
62-152
0-61 metres
0 10 20 30 km
0 5 10 15 20 miles


A.
B.
200 µm
200 µm
C.
200. µm
Camera
D.
50. µm
BSE Z
E.
50 µm
16 cm
F.
50 µm
56 cm
G.
50 µm
56 cm



Sluggan 56cm (This study)
Sluggan 46-51cm (This study)
Sluggan 30-35cm (This study)
Sandy Braes Obsidian (This study)
Davies, 2003 16cm (EDI)
Davies, 2003 16cm (BEL)
Davies, 2003 56cm (EDI)
Vedde Ash (RESET database)
Penifiler Tephra (RESET database)
Borrobol Tephra (RESET database)
Perlite (Sandy Braes; Patterson, 1952)
Porphyritic Obsidian (Sandy Braes; Cameron and Sabine, 1969)
Porphyritic Obsidian (Sandy Braes; Brooks et al., 1981)



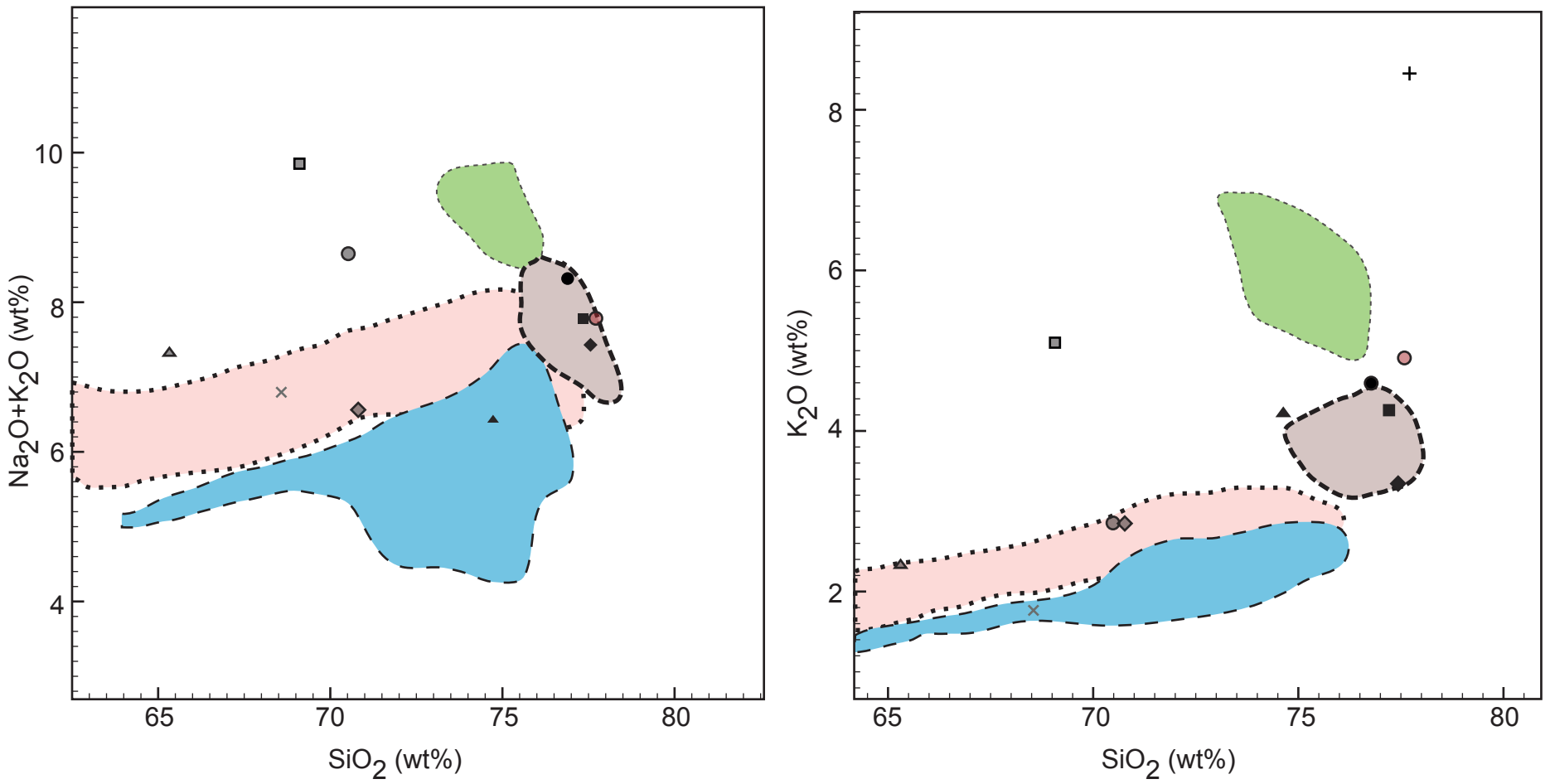
Revised probable LGM ice limit

Broad ice flow direction during the LGM

Ice flow directions during the LLS

Location of obsidian outcrops

LLS ice limits



Pitchstone data (Thorpe and Thorpe, 1984):

- Arran Corrygills, AP4
- Arran Glen Cloy, 823
- Eigg P1
- Raasay, RP1
- Arran Glen Shurig, AP6
- Ardnamurchan, ARDP1
- Eigg P2
- Sandy Braes
- Arran Tormore, AP1
- Ardnamurchan, ARDP3
- Mull, MP1

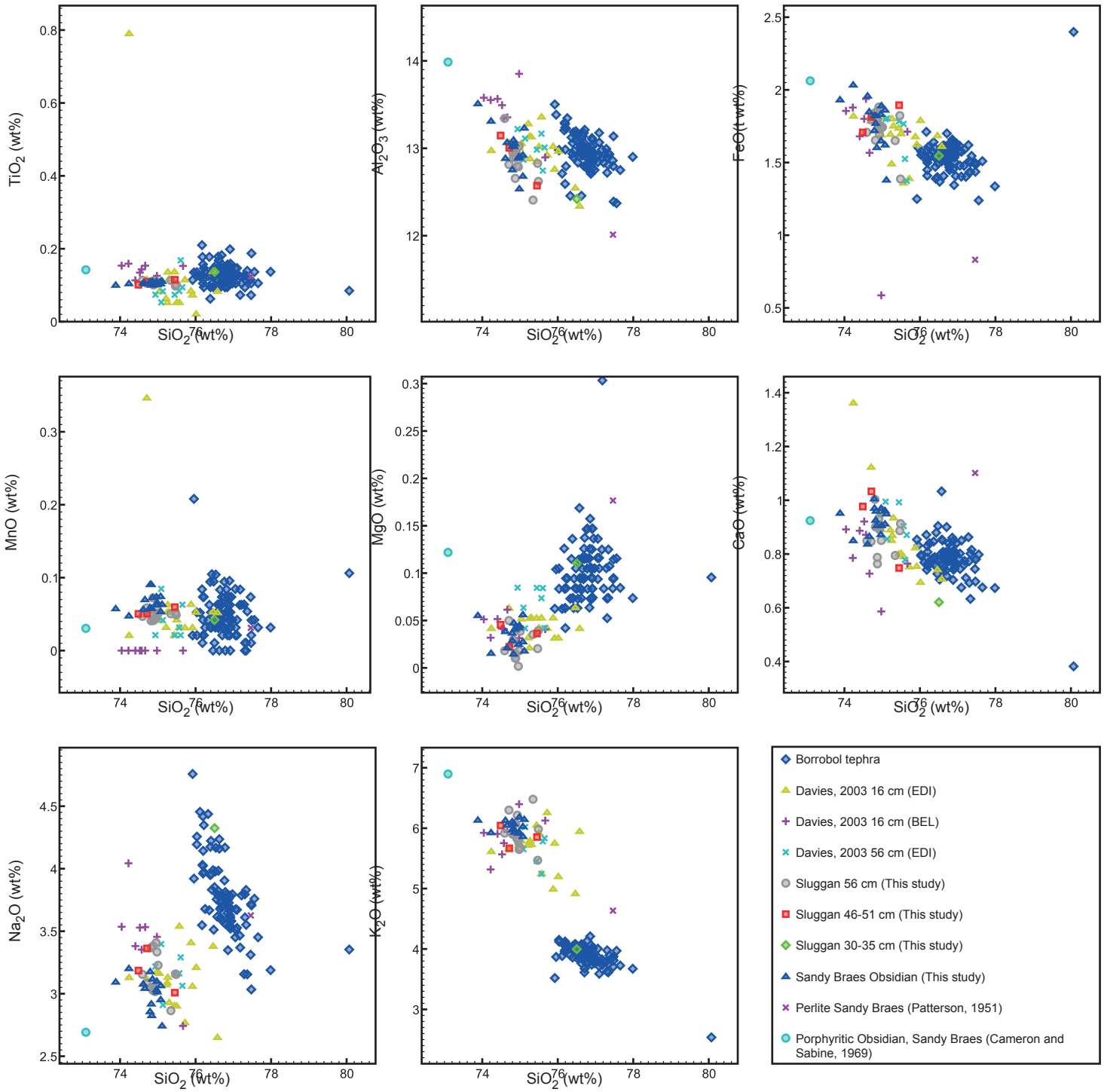
Chemical envelopes:

- Sluggan Bog 56, 16 cm and SBO data (Davies, 2003 and this study)
- Borrobol and Penifiler data (Bronk Ramsey et al., 2015)
- Hekla (Bronk Ramsey et al., 2015)
- Askja (Bronk Ramsey et al., 2015)

Tephra Analyitical Unit, Edinburgh University	
Electron Microprobe	Cameca SX-100, 5 Spectrometers
Element oxides analysed	Na, Al, Si, Fe, K, Ca, Mg, Mn, Ti, P, Cl, F
Accelerating volatage	15 keV
Beam current	2nA/80 nA
Beam diameter	5 µm
Primary/Secondary calibration	Standard calibration blocks/Lipari obsidian/STHS (data provided)
Electron Microscope Unit Queen's University, Belfast	
Electron Microprobe	Jeol 733 Superprobe, 4 Spectrometers
Elements analysed	Na, Al, Si, Fe, K, Ca, Mg, and Ti
Accelerating volatage	15 keV
Beam current	10 nA
Beam diameter	8 µm
Primary/Secondary calibration	Standard calibration blocks/Lipari obsidian

Sample	Element Oxides (wt%)												
	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	Total
16cm Davies (2003 - EDINBURGH)	72.59	0.08	12.63	1.75	0.04	0.05	0.93	3.06	5.60	-	-	-	96.74
	72.31	0.11	12.54	1.63	0.38	0.04	0.86	3.06	5.52	-	-	-	96.45
	73.67	0.08	11.87	1.55	0.05	0.04	0.68	2.55	5.72	-	-	-	96.20
	71.41	0.76	12.48	1.75	0.02	0.04	1.31	3.01	5.40	-	-	-	96.19
	72.47	0.11	12.37	1.33	0.03	0.04	0.72	2.65	5.99	-	-	-	95.71
	71.87	0.13	12.30	1.72	0.06	0.05	0.83	2.99	5.53	-	-	-	95.49
	72.47	0.07	12.18	1.55	0.03	0.03	0.72	2.92	5.49	-	-	-	95.46
	71.19	0.11	12.45	1.70	0.33	0.06	1.07	2.97	5.39	-	-	-	95.29
	71.66	0.05	12.51	1.42	0.05	0.02	0.81	2.94	5.48	-	-	-	95.23
	71.69	0.13	12.21	1.65	0.02	0.05	0.76	2.76	5.75	-	-	-	95.03
	72.23	0.02	12.32	1.70	0.05	0.03	0.66	3.05	4.94	-	-	-	95.02
	71.73	0.05	12.68	1.29	0.03	0.05	0.75	3.36	4.98	-	-	-	94.92
	71.56	0.05	12.34	1.61	0.04	0.04	0.76	2.75	5.61	-	-	-	94.78
	71.91	0.08	12.34	1.59	0.06	0.05	0.78	3.23	4.73	-	-	-	94.77
	71.02	*0.06*	*12.54*	*1.60*	*0.03*	*0.03*	*0.84*	*2.90*	*5.40*	-	-	-	*94.42*
	72.16	*0.13*	*11.84*	*1.59*	*0.05*	*0.06*	*0.70*	*3.19*	*4.64*	-	-	-	*94.37*
	70.94	*0.11*	*12.37*	*1.65*	*0.05*	*0.05*	*0.88*	*2.76*	*5.40*	-	-	-	*94.21*
16cm Davies (2003 – BELFAST)	74.23	0.15	12.65	1.68	-	0.04	0.75	2.69	6.01	-	-	-	98.10
	72.73	0.14	13.01	1.89	-	0.04	0.85	3.27	5.61	-	-	-	97.53
	72.91	0.15	13.04	1.53	-	0.06	0.71	3.45	5.80	-	-	-	97.65
	72.02	0.13	13.04	1.74	-	0.04	0.89	3.41	5.38	-	-	-	96.64
	72.18	0.11	13.16	1.63	-	0.05	0.86	3.28	5.73	-	-	-	97.01
	71.61	0.12	13.23	0.56	-	0.03	0.56	3.30	6.11	-	-	-	95.51
	69.94	*0.15*	*12.77*	*1.77*	-	*0.03*	*0.74*	*3.81*	*5.01*	-	-	-	*94.23*
	72.25	0.15	13.25	1.81	-	0.05	0.87	3.45	5.78	-	-	-	97.58
56cm Davies (2003 – EDINBURGH)	72.03	0.08	12.57	1.73	0.04	0.04	0.82	2.79	5.77	-	-	-	95.87
	72.11	0.09	12.40	1.31	0.06	0.04	0.83	2.92	5.56	-	-	-	95.32
	71.91	0.08	12.53	1.68	0.03	0.07	0.86	3.01	4.99	-	-	-	95.16
	71.90	0.16	12.12	1.45	0.02	0.08	0.74	3.13	5.50	-	-	-	95.10
	71.47	0.07	12.30	1.69	0.02	0.08	0.94	2.99	5.17	-	-	-	94.73
	70.96	0.05	12.16	1.70	0.08	0.06	0.94	3.21	5.34	-	-	-	94.50
	70.80	0.07	12.49	1.64	0.02	0.08	0.89	3.04	5.45	-	-	-	94.48
56cm (This study – EDINBURGH)	71.61	0.10	12.34	1.58	0.04	0.03	0.86	3.22	5.66	0.01	0.03	0.21	95.70
	72.72	0.10	12.52	1.72	0.04	0.01	0.87	2.96	5.90	0.01	0.03	0.24	97.11
	73.52	0.10	12.50	1.78	0.05	0.02	0.86	3.08	5.33	0.01	0.03	0.15	97.42
	72.22	0.11	11.89	1.58	0.05	0.03	0.76	2.75	6.21	0.01	0.03	0.20	95.86
	72.27	0.10	12.42	1.68	0.05	0.04	0.93	3.11	5.47	0.01	0.03	0.24	96.35
	72.69	0.10	12.58	1.80	0.05	0.02	0.76	2.94	5.90	0.00	0.03	0.21	97.08
	71.71	0.10	12.39	1.80	0.04	0.04	0.89	2.92	5.58	0.01	0.04	0.21	95.73
	71.68	0.10	12.41	1.76	0.05	0.03	0.96	2.92	5.65	0.01	0.03	0.21	95.83
	72.05	0.11	12.18	1.73	0.07	0.01	0.73	3.25	5.68	0.01	0.03	0.38	96.23
	72.99	0.10	12.68	1.70	0.05	0.02	0.83	3.25	5.50	0.02	0.03	0.18	97.35
	72.31	0.10	12.09	1.33	0.05	0.04	0.87	3.02	5.73	0.02	0.03	0.21	95.79
	72.50	0.11	12.97	1.66	0.05	0.02	0.83	3.07	5.75	0.01	0.03	0.22	97.19
	71.84	0.10	12.32	1.73	0.06	0.05	0.81	2.97	6.06	0.01	0.03	0.19	96.16
	71.14	0.11	12.14	1.65	0.04	0.00	0.86	3.23	5.49	0.02	0.03	0.19	94.91
	72.47	0.10	12.38	1.64	0.04	0.04	0.86	2.92	6.01	0.01	0.03	0.22	96.72
46-51cm (This study – EDINBURGH)	72.60	0.11	12.10	1.82	0.06	0.03	0.72	2.89	5.63	0.01	0.04	0.21	96.23
	71.24	0.10	12.57	1.63	0.05	0.04	0.93	3.05	5.78	0.02	0.03	0.19	95.65
	71.38	0.10	12.42	1.73	0.05	0.02	0.99	3.21	5.41	0.01	0.03	0.17	95.54
30-35cm (This study – EDINBURGH)	72.71	0.13	11.80	1.47	0.04	0.10	0.59	4.11	3.80	0.01	0.14	0.13	95.04

Sample	Element Oxides (wt%)												
	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	Total
Sandy Braes Obsidian (This study – EDINBURGH)	73.02	0.11	12.55	1.78	0.07	0.02	0.85	2.95	5.76	0.01	0.03	0.24	97.40
	74.11	0.10	12.52	1.84	0.07	0.03	0.90	2.91	5.95	0.02	0.03	0.24	98.72
	72.42	0.10	12.60	1.76	0.06	0.05	0.93	2.73	5.88	0.01	0.03	0.20	96.77
	72.85	0.11	12.70	1.56	0.07	0.04	0.88	3.03	5.77	0.03	0.03	0.24	97.31
	72.96	0.10	12.56	1.60	0.06	0.04	0.94	3.02	5.78	0.02	0.02	0.21	97.31
	72.92	0.10	12.69	1.68	0.06	0.04	0.98	2.79	5.95	0.01	0.03	0.24	97.49
	72.34	0.10	12.97	1.98	0.05	0.02	0.83	3.12	5.77	0.01	0.02	0.23	97.45
	72.60	0.10	12.70	1.72	0.09	0.01	0.90	2.83	5.81	0.01	0.03	0.22	97.02
	72.61	0.10	12.14	1.83	0.06	0.04	0.88	2.92	5.99	0.00	0.02	0.24	96.83
	72.97	0.11	12.85	1.34	0.06	0.02	0.92	2.66	5.97	0.00	0.02	0.20	97.14
	71.71	0.10	12.55	1.78	0.07	0.02	0.83	2.92	5.81	0.01	0.03	0.21	96.05
	72.56	0.11	12.37	1.77	0.09	0.03	0.94	3.08	5.80	0.01	0.02	0.23	97.01
	71.12	0.10	13.00	1.86	0.06	0.05	0.92	2.98	5.90	0.01	0.03	0.24	96.26
	72.16	0.10	12.46	1.89	0.05	0.04	0.81	2.98	5.93	0.01	0.03	0.25	96.71
	71.99	0.11	12.39	1.55	0.05	0.05	0.92	2.94	5.62	0.02	0.02	0.22	95.88
Lipari Standard (Mean n=14)	73.97	0.08	13.07	1.56	0.07	0.04	0.74	4.05	5.18	0.01	0.37	0.19	99.32
Lipari Standard (1 Std dev n=14)	0.45	0.00	0.14	0.06	0.01	0.01	0.04	0.14	0.10	0.00	0.01	0.01	0.61
STHS Standard (Mean n=3)	63.68	0.73	17.79	4.44	0.08	1.94	5.26	4.75	1.34	0.15	0.02	0.03	100.20
STHS Standard (1 Std dev n=3)	0.58	0.01	0.17	0.03	0.00	0.08	0.03	0.08	0.02	0.01	0.00	0.01	0.57


TiO2 (wt%)
Al2O3 (wt%)
FeOt (wt%)
MnO (wt%)
MgO (wt%)
CaO (wt%)
Na2O (wt%)
K2O (wt%)
SiO2 (wt%)
Borrobol tephra
Davies, 2003 16 cm (EDI)
Davies, 2003 16 cm (BEL)
Davies, 2003 56 cm (EDI)
Sluggan 56 cm (This study)
Sluggan 46-51 cm (This study)
Sluggan 30-35 cm (This study)
Sandy Braes Obsidian (This study)
Perlite Sandy Braes (Patterson, 1951)
Porphyritic Obsidian, Sandy Braes (Cameron and Sabine, 1969)