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Identification of the Askja-S Tephra in a rare turlough record from Pant-y-Llyn, south Wales

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Abstract

Tephrochronology and especially crypto-tephrochronology is an established chronological technique employed in a range of depositional environments in Europe and beyond. During the late Quaternary, Icelandic cryptotephra deposits are widely found in palaeorecords across northern latitudes of Europe e.g. Scotland, Ireland, Norway, Sweden and the Faroe Islands but are sporadic in southerly latitudes as distance from Iceland increases. As yet, very few Icelandic cryptotephras have been identified in Wales or southern England which may well reflect the geographical limit of Icelandic tephra distribution. Here, however, we report the discovery of an Icelandic cryptotephra deposit within a sediment sequence retrieved from the Pant-y-Llyn turlough (Carmarthenshire, south Wales), the only known turlough in Britain. Turloughs are groundwater-fed ephemeral lakes associated with limestone bedrock and can accumulate sediments that may yield records suitable for palaeoreconstructions. A discrete peak of glass shards originating from the Askja-S eruption is identified in the sediment record. This discovery extends the distribution of this early Holocene eruption giving new insight into its dispersal patterns and also indicates that sedimentary sequences from sites in these more southerly latitudes are valuable repositories for ash preservation. Furthermore, its discovery within a carbonate-rich sequence provides a minimum age constraint on the timing of sediment accumulation and provides an alternative tool for what is typically a problematic dating environment.

1. Introduction

Tephrochronology is a powerful dating technique whereby geochemically distinct and well-constrained ash deposits can underpin a chronological framework as well as allow precise and direct synchronisation of geological records (Lowe, 2011). In recent years, this technique has significantly progressed beyond the realms of visible or macro-ash deposits to focus on cryptotephra deposits preserved in distal areas relative to the volcanic source (Davies, 2015). Cryptotephra deposits are invisible to the naked eye and contain a low concentration of volcanic glass shards that can only be detected by microscopy following a series of extraction steps to isolate the shards from the host sediment. Discrete horizons were identified in distal peat bog deposits as early as the 1960s, where stratigraphic information was employed to suggest the preservation of the Hekla 3, Hekla 4, Askja 1875 and Öraefajökull 1362 cryptotephras in Swedish, Norwegian and Faroes peat bogs (Persson, 1966, 1971). It was the discovery of cryptotephra in Scottish peat (Dugmore, 1989), however, that instigated the recent advances in the search for ash deposits far removed from volcanic centres.

Extensive employment of extraction techniques such as ashing (for organic rich deposits; Dugmore, 1989) and density separation (for minerogenic sediments; Turney, 1998) together with robust chemical characterisation of glass shards (Hayward, 2012) have given rise to an abundant European network of cryptotephra discoveries (Fig. 1). Traces of Icelandic eruptions spanning the last 15,000 years have been identified in depositional records across Europe (e.g. Wastegård and Davies, 2009; Lawson et al., 2012; Davies et al., 2012; Timms et al., 2016; Wulf et al., 2016). However, there are very few reported findings of distal ash deposits south of 53^0 latitude and east of 6^0 longitude and noticeable gaps in Wales, southern England and large parts of France are evident on spatial distribution maps (Fig. 1). The density of cryptotephra discoveries is also skewed towards the sites located in northerly latitudes with only the largest known eruptions such as the Vedde Ash and the Askja-S Tephra found in more southerly latitudes (e.g. Lane et al., 2011, 2012b). This apparent absence may be an indicator of the geographical limit of most Icelandic ash plumes but most likely reflects a sampling bias with very few studies conducted in lowland areas of Wales and southern England. With the exception of a recent study by Watson et al., (2017), there have been traces of potential cryptotephra deposits identified in sites in the Brecon Beacons and mid-Wales but these findings have not been supported by geochemical characterisation of the shards themselves (Williams, 2001; Williams et al., 2007; Buckley and Walker, 2002).

Here we explore tephra preservation in a sediment sequence extracted from the Pant-y-Llyn turlough in south Wales (Fig. 2). Turloughs are ephemeral water bodies associated with topographic depressions in karst and are periodically inundated mainly by groundwater. Turloughs are common in the Republic of Ireland (Skeffington et al., 2006; Naughton et al., 2012), however, this is the only known turlough in Britain (Campbell et al., 1992; Hardwick and Gunn, 1995) and as such is a designated Annex I priority habitat under the EU Habitats Directive 92/43/EC (McLeod et al., 2005). Turloughs do not have a true inflow or outflow stream, and fill and empty either diffusely across their base or via estavelles, a karst feature that can act as both a spring and a sink (Tynan et al., 2007). Sediments from turloughs are rich in calcium carbonate (Coxon and Coxon, 1994) and an investigation of their infill can provide insight into the development and formation of these rare features. Dating such sedimentary sequences using the conventional radiocarbon method, however, is problematic due to the erroneous effects of hard-water and contamination by old carbon (Lowe and Walker, 2000). Tephra deposits have huge potential as an alternative dating technique for such sequences (e.g. Candy et al., 2016; Timms et al., 2016) and we present the first positive findings in Wales to date a carbonate-rich record retrieved from a turlough.

2. Site Description and Methods

The Pant-y-Llyn turlough is located in south Wales, UK (Lat: 51^0 49’ 51” N, Long: 4^0 1’ 26” W) at an altitude of 150 m OD. The lake is small, just 160 m long and 60 m wide, and lies in a depression formed in the underlying Carboniferous Dowlais Limestone Formation (Fig. 2).

Sediment cores were obtained on 28th August 2013 when water levels were sufficiently low to allow access into the turlough basin. A basin survey was conducted using a peat probe and hand auger at 10 locations to determine the area with the thickest sequence of soft sediment. Using a Russian corer (5 cm diameter, 50 cm length) a 550 cm core was obtained from the eastern part of the turlough basin, but the bedrock was not reached (Fig. 2). The core (British Geological Survey borehole reference SN61NW12) is comprised of a sequence of unconsolidated lake muds, silts and peat. Cores were wrapped in cling film and stored in a cold room at <4 ^{0}C until sub-sampling was undertaken. Four 100 g bulk sediment samples from 200, 245, 395, 510 cm depth below ground level were sent to the ^{14}CHRONO Centre at Queens University Belfast for dating (Table. 1).

Loss on ignition (LOI) was conducted on the core between 550-300 cm. LOI was performed at a 4-cm resolution between 550-530 cm and 490-300 cm and at a 2-cm resolution between 530-490 cm spanning the transition from the basal unit of reddish silty clay and organic lake mud unit. The standard protocol of Heiri et al., (2001) was followed with samples placed in a furnace at 550 ^{0}C for 2 hours to determine the organic matter loss by weight percent and a further 2 h at 1000 ^{0}C to determine the calcium carbonate ($CaCO_3$) loss by weight percent.

Tephra investigations focused on the 350-550 cm portion of the sequence with initial searches conducted on 5-cm contiguous samples and followed the methodology outlined in Turney, (1998). The samples were ashed at 550 ^{0}C for 2 hours and the remaining particulate material was sieved at 80 and 25 µm. Due to the minerogenic nature of the sediment a density separation was performed using sodium polytungstate and the 2.3-2.5 gcm^{-3} density fraction was mounted onto microscope slides using Canada Balsam. A light-powered, polarizing microscope was used at x100 and x200 magnification to identify and count the glass shard concentrations. Where a distinct peak in tephra shard concentration was present, 1-cm segments were sub-sampled from the core to pinpoint the position of the tephra isochron to the nearest cm. For geochemical analysis, samples were processed following the same methodology as outlined above, with the exception of the ashing step. Due to the low shard concentrations a micro-manipulator was used to extract individual shards for geochemical analysis. Shards were placed on a microprobe slide and embedded in epoxy resin. Glass shards were sectioned using decreasing grades of silicon carbide paper and polished using 9, 6 and 1 µm diamond suspension and 0.3 µm micro-polish.

Geochemical analysis was undertaken at the Tephra Analytical Unit at the University of Edinburgh using a Cameca SX100 wavelength dispersive spectrometer electron-probe micro analysis (WDS EPMA). Operating conditions are noted in the supporting information. A 3 µm beam set-up was used for some shards due to the small particle size (Hayward, 2012). No analytical offsets were observed between the 3 and 5 µm set-ups (see supporting information). Lipari and BCR2g secondary standards were analysed at regular intervals to examine the accuracy of the instrument and the precision of the analysed tephra shards (see supporting information).

3. Results

3.1. Lithostratigraphy, LOI and radiocarbon dates

The lithostratigraphy is shown in Fig. 3, and consists of a basal unit of reddish silty clay (550-522 cm) overlain by grey silty clay (522-511 cm). An organic lake mud is present between 511 and 450 cm and is overlain by brown, carbonate-rich mud that shows some evidence of fine laminations (450-362 cm). These are not thought to be annually resolved. Organic fen peat is found in the uppermost part of the sequence (362-0 cm). LOI values are low (~12 %) within the basal clay unit indicating a high minerogenic input which we suggest has been deposited during the Loch Lomond Stadial. Calcium carbonate values also remain low (~5 %) within this unit. A sudden increase in LOI values is observed at 511 cm, reaching values of 50 % by 508 cm. We suggest that this may represent the early Holocene transition. The highest LOI values (55-70 %) are observed between 500 and 466 cm with a shift towards slightly lower values of around 50 % between 466 and 430 cm. Calcium carbonate values begin to increase at around 480 cm but show marked fluctuations between 10 and 40 % between 480 and 430 cm. A short-lived peak of 70 % in calcium carbonate content is observed at 422 cm and is accompanied by a dip in LOI at the same depth. Between 410 and 360 cm, low LOI values (10-25 %) are accompanied by higher calcium carbonate values (60-76 %). The increase in LOI values and corresponding decrease in calcium carbonate values observed 360 cm (47 % and 10 % respectively) coincides with a shift from lake mud to fen peat. In the uppermost part of the record, LOI increases to ~60 % at 335 cm and calcium carbonate content falls to ~10 % (Fig. 3). The overall calcium carbonate variations in this sequence may reflect periods of stronger groundwater influence in this turlough.

Radiocarbon ages obtained from four bulk samples are summarised in Table 1. The lowermost radiocarbon date lies stratigraphically at the base of the lake mud unit, which is assumed to represent the early Holocene. However, the radiocarbon age estimate reveals a much older age of 12958-12713 cal BP which is closer to the onset of the Loch Lomond Stadial. Similarly, an age range of 12589-12105 cal BP is obtained for the sample at 395 cm, which lies 115 cm above the lowermost radiocarbon age, implying a relatively high sedimentation rate (7 yrs/cm) compared with other similar sediment deposits of this age (e.g. Quoyloo Meadow - ~46 yrs/cm: Timms et al., 2016). The uppermost ages at 200 and 245 cm are also close in age (~8.7 cal BP and ~8.6 cal BP, respectively) and indicate a slight inversion with the former yielding an older age than the latter (Table. 1).

3.2. Tephra discoveries

Low-resolution investigation of the tephra content revealed the presence of one distinct peak in shard concentration at 495-500 cm whilst the rest of the sequence revealed a low background of ~ 2-3 glass shards per 0.5 gram dry weight (g dw) at intermittent intervals. Due to the low shard concentrations, no geochemical results were attempted and without this information, the significance of the apparent background in glass shards is uncertain. The distinct peak in shard concentration between 495-500 cm was refined to 1 cm where a concentration of 72 shards per 0.5 gram dry weight (g dw) was established at 499-500 cm (labelled PLL_500 in Fig 3 and 4). The shards were colourless and typically platy and fluted in morphology. Microprobe analyses confirm their homogenous rhyolitic composition with SiO_2 values ranging between 72.24 - 76.4 wt%, K_2O values of 2.39 – 2.65 wt% and CaO values of 1.5 – 1.75 wt% (Table 2). Major oxide biplots reveal a strong correlation with the

Askja-S Tephra (Fig. 4) which can easily be distinguished from other early Holocene age tephras such as the Hässeldalen Tephra on the basis of higher FeO and CaO values (Fig. 4). The tephra at Pant-y-Llyn is also geochemically distinct relative to other early Holocene tephras including the Suðuroy, An Druim, Breakish, Hovsdalur, Høvdarhagi, L274, Skopun, Fosen, Ashik and Abernethy tephra (Fig. 4) (Wastegård, 2002; Ranner et al., 2005; Pyne O'Donnell, 2007; Lind and Wastegård, 2011; Matthews et al., 2011; Lind et al., 2013). The Askja-S geochemical signature can also be discriminated from older widespread tephras such as the Vedde Ash based on higher SiO_2 and CaO values.

Whilst chemical similarity is shown between the Askja-S Tephra and the 499-500 cm deposit, the radiocarbon dates would suggest an older age than presently suggested for the Askja-S Tephra. It is possible that PLL_500 could be a previously unknown tephra originating from the Dyngjufjöll volcanic system, given the closely timed tephra deposits of similar chemical signatures derived from Icelandic provenances, such as Katla (Lane et al., 2012b) or the numerous Borrobol-type deposits discovered (Lind et al., 2016; Jones et al., 2017). As yet, however, there are no reported findings of older Askja-S-type tephras in the literature. Guðmundsdóttir et al., (2016) have reported a younger tephra – the Askja L– dated to approximately 9400 cal BP (Striberger et al., 2012) and the Askja H tephra – dated to 8850 years old has been identified by Jóhannsdóttir, (2007). The former tephra reveals an identical chemical composition to Askja-S but the Al_2O_3 and FeO content for the latter differs from the Askja-S (Guðmundsdóttir et al., 2016). The Askja L and H have, however, never been discovered outside of Iceland making the Askja-S correlation most likely in Pant-y-Llyn. The lithostratigraphic information also supports this correlation to the early Holocene Askja-S Tephra in line with other studies (e.g. Davies et al., 2003; Wulf et al., 2016; Timms et al., 2016).

4. Discussion

4.1. Askja-S Tephra dispersal and significance

The identification of the Askja-S Tephra in the Pant-y-Llyn record, extends the geographical area of Icelandic ash deposition. Until now, very few Icelandic tephras have been found south of 53^0 latitude and east of 6^0 longitude (Fig. 1) and our new findings indicate that this is not a reflection of the dominance of more northerly dispersal trajectories (see also recent findings outlined by Watson et al., 2017). We propose potential dispersal maps based on reported Askja-S findings and, given the reported negative findings for this tephra (Table 3 and Fig 5c), speculate that dispersal may have been characterised by more than one plume trajectory (Fig. 5c). Proximal deposits in Iceland, however, suggest the main axis of Askja-S dispersal was mainly to the NNE (Sigvaldason et al., 2002). We acknowledge that several other factors may also account for the absence of the Askja-S Tephra in some records (e.g. uneven ash distribution within sites, failure to pinpoint cryptotephra deposits in low-resolution searches; Pyne O'Donnell, 2011; Timms et al., 2016), however, we use our maps to highlight geographical areas that are most likely to result in fruitful recovery of the Askja-S deposit. In particular, the relatively high shard concentrations (72 shards per 0.5 gdw) highlight the tantalising possibilities of tracing the Askja-S Tephra, as well as other Icelandic tephras, further south in the British Isles and perhaps France.

4.2. Askja-S age estimate

The Askja-S Tephra is considered to be a key isochronous marker for the early Holocene and its extensive distribution from Arctic Norway (Pilcher et al., 2005) to Switzerland (Lane et al., 2011) and from northern Ireland (Turney et al., 2006) to north Poland (Wulf et al., 2016) now allows Pant-y-Llyn to be precisely integrated within a broad palaeorecord network (Fig. 5). One age estimate for the Askja-S Tephra is 10,830±57 cal BP, which was derived by age-modelling a range of radiocarbon dates (Bronk Ramsey et al., 2015 and references within), however, Ott et al., (2016) provide an older age of 11,228±26 cal BP based on a varve-interval from the Hässeldalen tephra in Lake Czechowskie, Poland. Based on the relative stratigraphic positions of tephras in the Lake Hämelsee record, Jones et al (2017) suggests that the Ott et al., (2016) age estimate is marginally too old than the age estimate outlined by Bronk Ramsey et al., (2015).

In the Pant-y-Llyn sequence, the radiocarbon date at 510 cm (10 cm below the Askja-S Tephra) has revealed an age range of 12,958-12,713 cal BP, almost ~2000 years older than the Askja-S Tephra. A further date of 12589–12105 cal BP is obtained from the sample dated at 395 cm (Table 1 & Fig. 3). Given the hard-water error that affects sediments in limestone terrain (Walker, 2005), we suggest that these ages cannot be used to obtain a reliable age-model, especially the sample obtained from 395 cm where $CaCO_3$ content is 68 %. The discrete Askja-S peak, however, provides a well-constrained age marker for the lowermost part of the sequence and constrains the brown gyttja to the early Holocene interval. Although bedrock was not reached during coring, the Askja-S Tephra provides a minimum age estimate for the sediment sequence and indicates that the underlying silty clay unit is likely to represent the Loch Lomond Stadial. Further work will need to ascertain whether a full Late-glacial sequence is preserved at the site; such records are limited in number in south Wales (e.g. Walker et al., 2003, 2009).

5. Conclusion

The identification of the Askja-S Tephra in the Pant-y-Llyn turlough sediments extends the known distribution of this tephra further south and east in the British Isles and suggests that sites south of 53^0 latitude and east of 6^0 longitude can be valuable repositories for ash preservation. We compile positive and negative findings of the Askja-S Tephra and use this distribution to propose a three plume trajectory. The independently dated age estimate for the Askja-S Tephra (10,830±57 cal BP – Bronk Ramsey et al., 2015) provides a crucial chronological marker for this record and provides a minimum age estimate for the onset of sediment accumulation at Pant-y-Llyn. This study highlights the value of using cryptotephra deposits to overcome the problems of radiocarbon dating sediment in limestone terrain. The lowermost silty clay deposit at Pant-y-Llyn is likely to have been deposited during the Loch Lomond Stadial and highlights the potential of extracting a palaeoenvironmental record from this sequence that extends back into the Late-glacial period. Further analysis of this core sequence may yield information on the evolution and formation of this rare turlough.

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Appendix A. Supporting Information

Supplementary material related to this article can be found in the online version.

Table 1. Four radiocarbon dates measured from bulk sediment at 14CHRONO Centre at Queens University Belfast. Ages were calibrated using OxCal and the IntCal13 calibration set (Bronk Ramsey, 2009; Reimer et al., 2013). Acid-Alkali-Acid (AAA) pre-treatment was undertaken on samples. Dates supplied by the British Geological Survey.

Laboratory ID code	Depth (cm)	δ^{13}C ‰	14C age yrs BP	Calibrated age range (cal BP)(95.4%)
UBA-26393	200	-25.4	7857±41	8932–8545
UBA-26392	245	-23.4	7833±37	8748–8541
UBA-26394	395	-26.8	10479±65	12589–12105
UBA-26391	510	-29.1	10953±47	12958–12713

Table 2. Summary geochemical data displayed as major oxide concentrations (average and standard deviation) for the tephra layer 499-500 cm (PLL_500). A complete list of analyses and full microprobe operating conditions can be found in the supplementary data.

	SiO_2	**TiO_2**	**Al_2O_3**	**FeO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**Total**
499-500 cm						**wt %**					
average (n=33)	*73.86*	*0.30*	*11.81*	*2.50*	*0.09*	*0.24*	*1.63*	*4.28*	*2.51*	*0.04*	*97.25*
st dev	*0.79*	*0.01*	*0.30*	*0.09*	*0.01*	*0.03*	*0.06*	*0.17*	*0.06*	*0.01*	*1.02*

Table 3. A compilation of positive and negative findings of the Askja-S Tephra (ordered by publication date). the sampling interval, age models and the stratigraphic position of other tephras in the original studies

Site	**Latitude and Longitude**	**Numer in Fig 5**	**Reference**
Lake Hämelsee, Germany	52°45' N, 9°18' E	1	Jones et al., 2017
Turret Bank, Scotland	57°00' N, 4°44' E	2	Lowe et al., 2017
Inverlair, Scotland	56°52' N, 4°43' W	3	Kelly et al., 2016
Quoyloo Meadow, Scotland	59°03' N, 3°18' W	4	Timms et al., 2016
Lake Tiefer See, Germany	53°35' N, 12°31' E	5	Wulf et al., 2016
Lake Czechowskie, Poland	53°52' N, 18°14' E	6	Wulf et al., 2016
Meerfelder Maar, Germany	50°06' N, 6°45' E	7	Lane et al., 2015
Store Slotseng basin, SW Denmark	55°19' N, 9°16' E	8	Larsen & Noe-Nygaard, 2014
Grønlia fen, Norway	63°47' N, 10°28' E	9	Lind et al., 2013
Wegliny, Poland	51°49' N, 14°43' E	10	Housley et al., 2013
Mulakullegöl, Sweden	57°12' N, 13°25' E	11	Lilja et al., 2013
Tøvelde, Denmark	54°57' N, 12°17' E	12	Larsen, 2013
Endinger Bruch, Germany	54°14' N, 12°53' E	13	Lane et al., 2012
Havnardalsmyren, Faroe Islands	62°01' N, 6°84' W	14	Kylander et al., 2012; Wasteg comm
Abernethy Forest, Scotland	57°14' N, 3°42' W	15	Matthews et al., 2011
Soppensee, Switzerland	47°05' N, 8°05' E	16	Lane et al., 2011
Høvdarhagi bog, Faroe Islands	61°54' N, 6°55' W	17	Lind & Wastegård, 2011
Loch Achik, Scotland	57°15' N, 5°50' W	18	Pyne O'Donnell, 2007
Lough Nadourcan, northwest Ireland	55°03' N, 7°54' W	19	Turney et al., 2006
Long Lough, Northern Ireland	54°26' N, 5°55' W	20	Turney et al., 2006
Borge Bog, Arctic Norway	68°14' N, 13°44' E	21	Pilcher et al., 2005
Hässeldala port, Sweden	56°16' N, 15°03' E	22	Davies et al., 2003

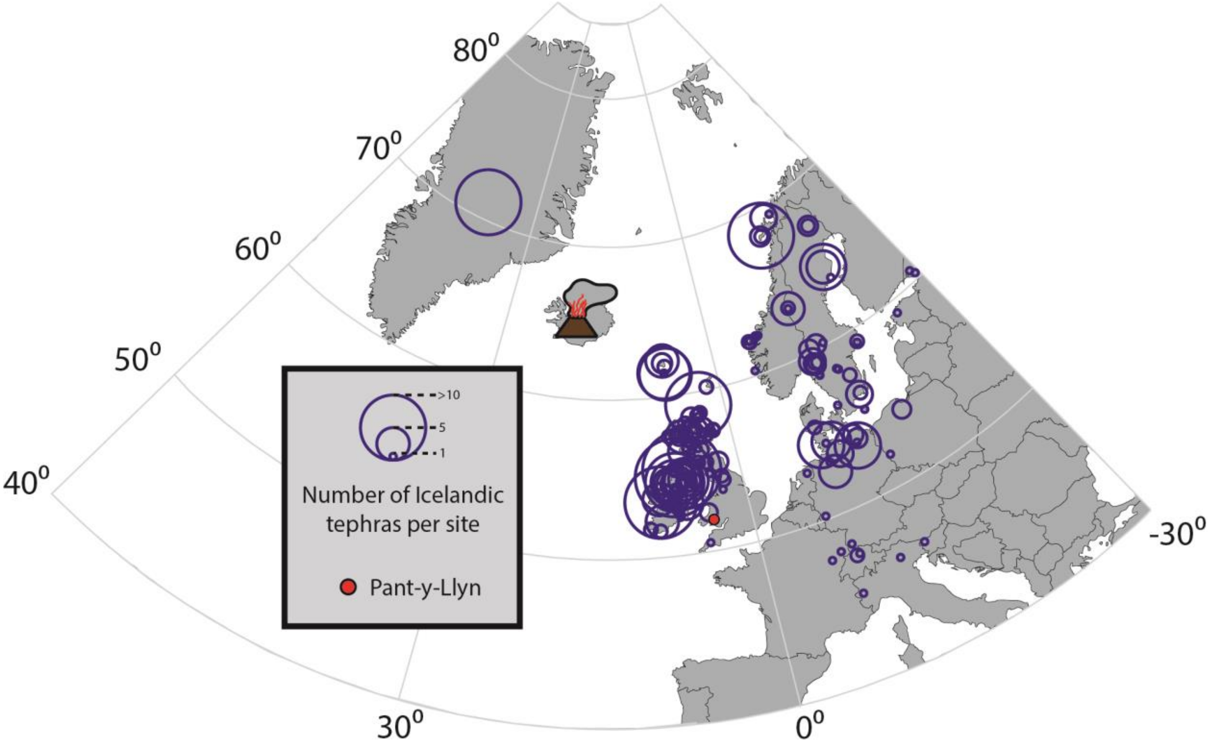

Figure 1. Spatial distribution map of Europe including distal sites (outside of Iceland) that contain Icelandic tephra layers of Holocene and Lateglacial age (~15 ka yr BP to present). Circle size relates to the number of tephra layers found in each site. Data from published sources (Davies et al., 2012; Lawson et al., 2012; Wulf et al., 2016; Watson et al., 2017; and references within). The circle on Greenland corresponds to the SUMMIT cores and NGRIP (Grönvold et al., 1995; Mortensen et al., 2005). Only one record in Wales has reported geochemical results to support tephra findings (Watson et al., 2017).

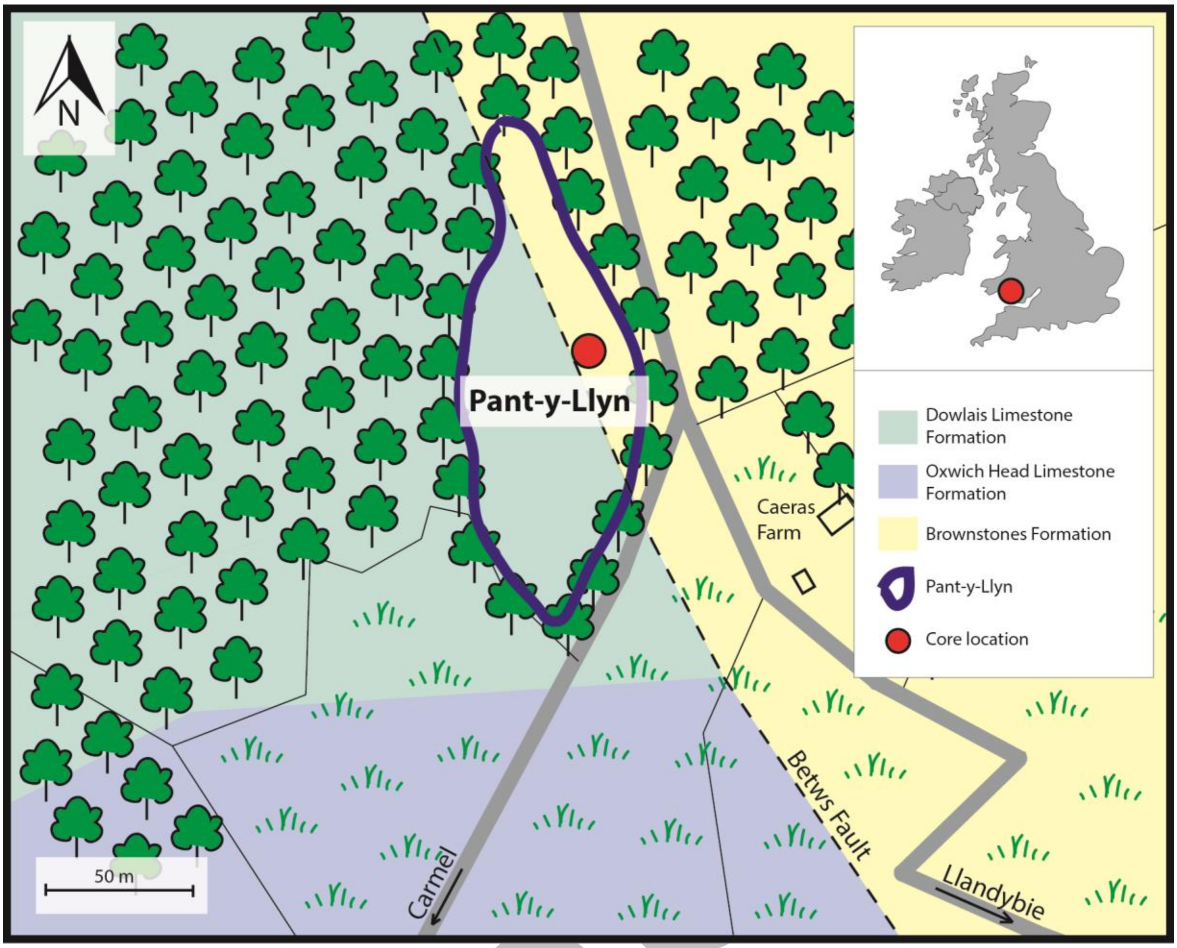

Figure 2. Location map of the Pant-y-Llyn turlough (Lat: 51^0 49' 51", Long: -4^0 1' 26"), coring location and local bedrock geology. 'Contains British Geological Survey Digi Map 1:50,000 Bedrock Geological Map and Ordnance Survey data © Crown Copyright and database rights 2017.

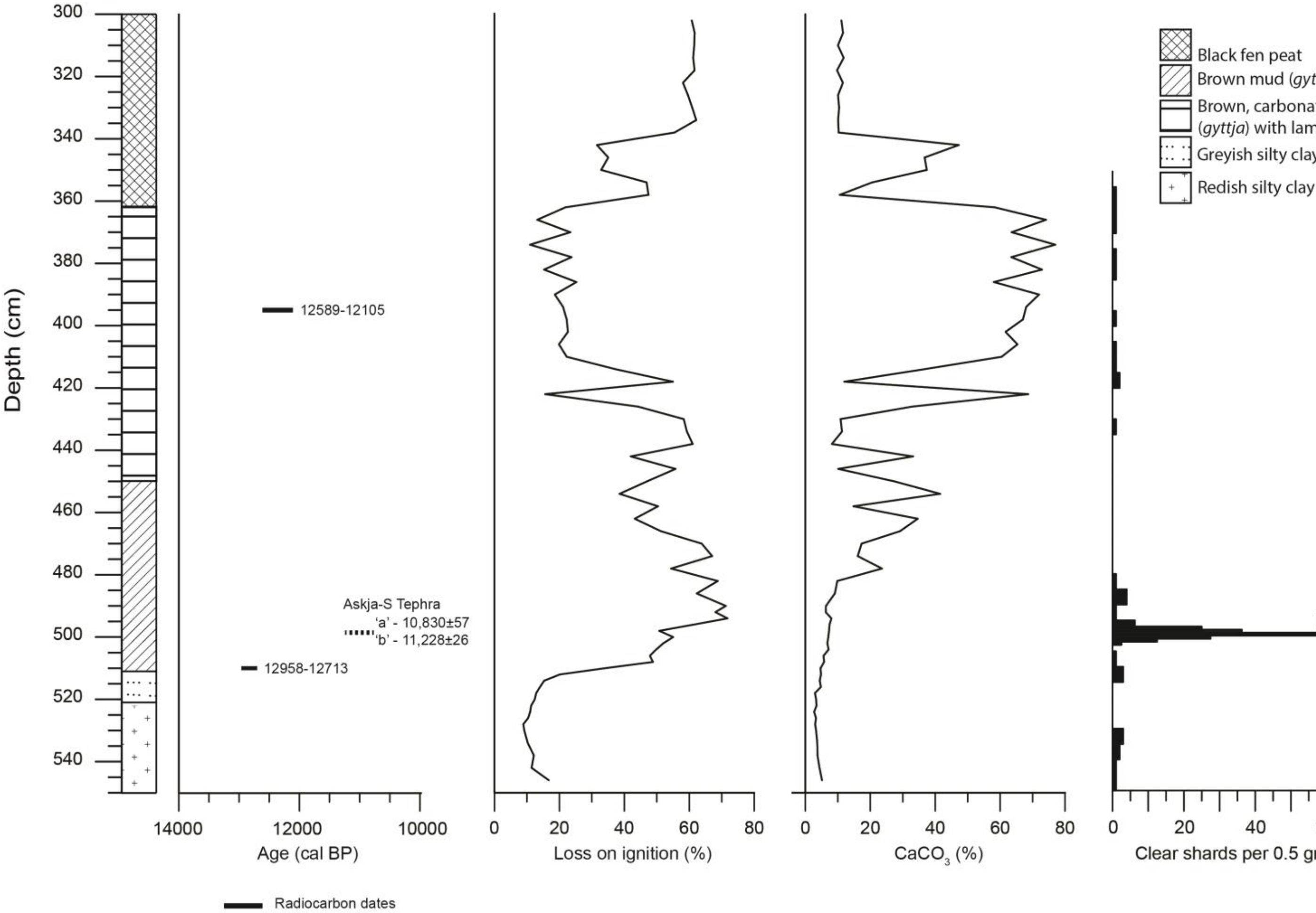

Figure 3. Lithostratigraphy, radiocarbon dates, loss on ignition, $CaCO_3$ content and total shard concentratio Borehole reference SN61NW12). Radiocarbon dates are derived from bulk sediment samples. Calibrated ag outlined in table 1. Askja-S Tephra age estimates are from Bronk Ramsey et al., 2015 (a) and Ott et al., 201

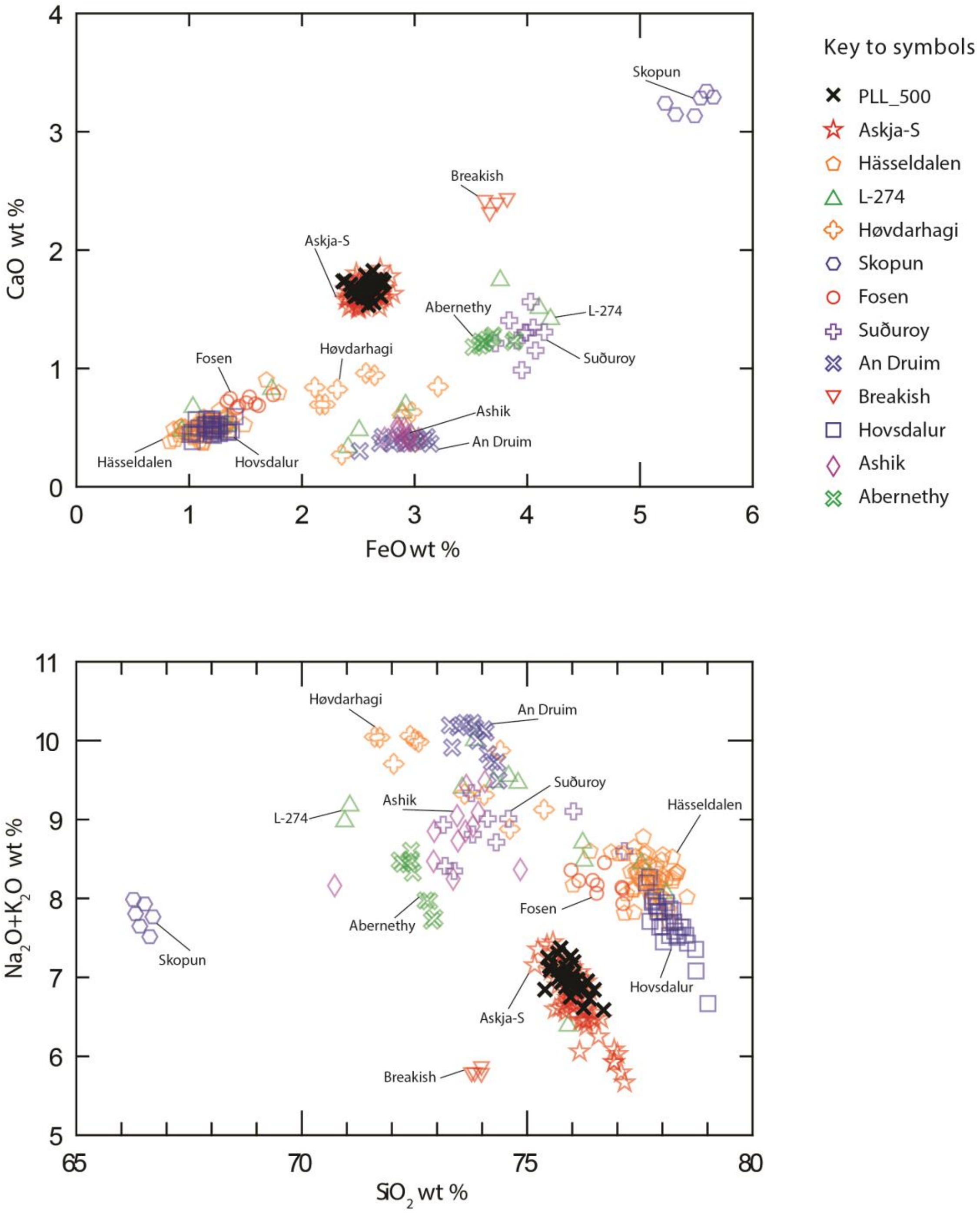

Figure 4. Selected bi-plots showing tephra PLL_500 glass shard major element composition correlating to the Askja-S Tephra. Hässeldalen, L-274 ,Høvdarhagi, Skopun, Fosen, Suðuroy, An Druim, Breakish, Hovsdalur, Ashik and Abernethy Tephra data also shown for discrimination. Data have been normalised. Data from: (Wastegård, 2002; Ranner et al., 2005; Pyne O'Donnell, 2007; Lind & Wastegård, 2011; Matthews et al., 2011; Lane et al., 2011, 2012a; Lind et al., 2013; Lilja et al., 2013; Wulf et al., 2016; Timms et al., 2016 and Jones et al., 2017).

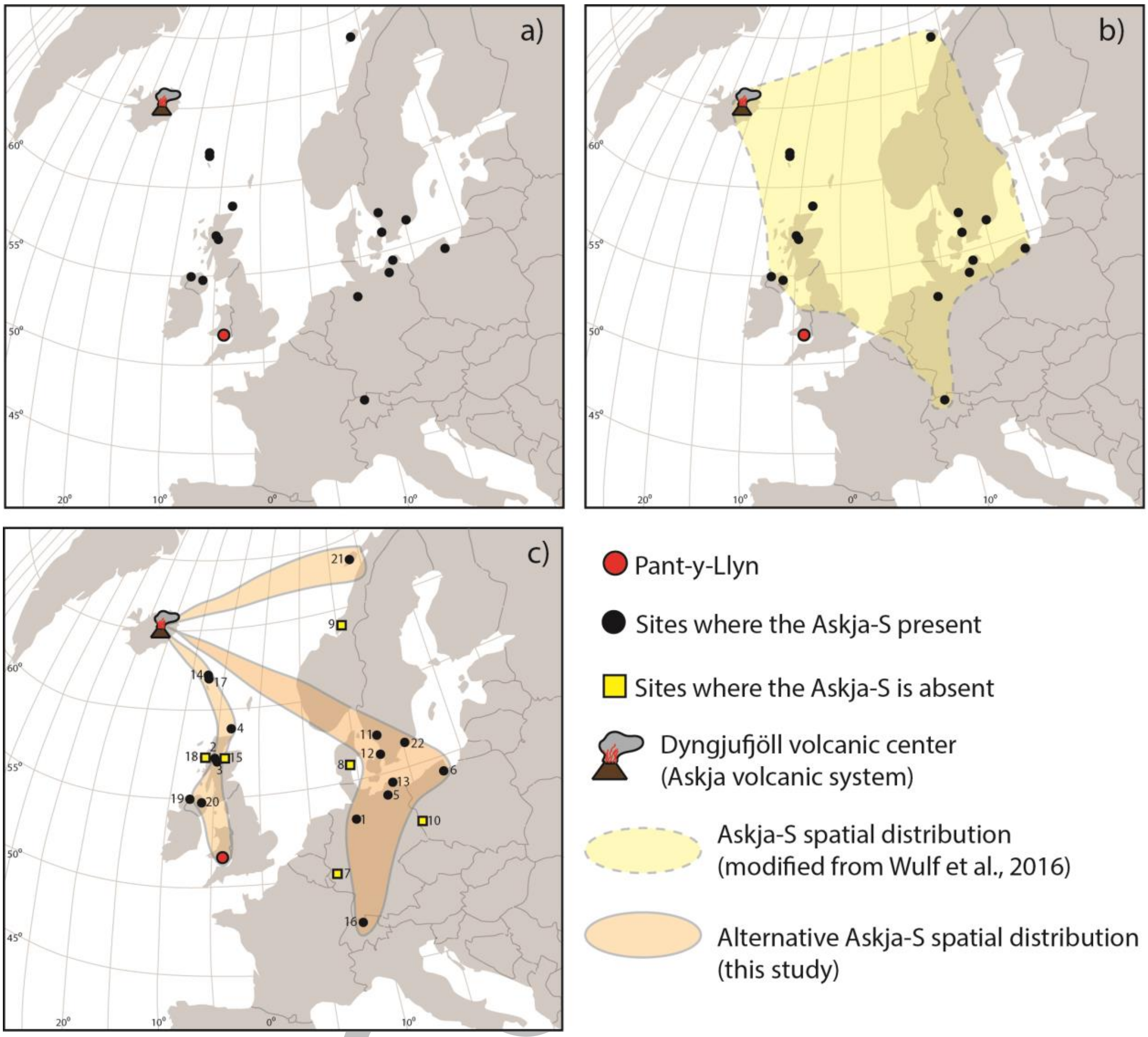

Figure 5. Spatial distribution maps for the Askja-S Tephra. a) Sites where the Askja-S Tephra is present. b) Current spatial distribution envelope for the Askja-S Tephra (modified from Wulf et al., 2016). c) Suggested plume trajectory, given the location of sites where the Askja-S is present and absent. Site numbers and details are provided in full in Table 3.

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