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1 **Standard chemical-based tephra extraction methods**
2 **significantly alter the geochemistry of volcanic glass**
3 **shards**

4

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23 *basaltic*

1 **Abstract**

2 The chemical compositions of tephra shards are widely utilised in a myriad of
3 disciplines, including volcanology, petrology, tephrochronology, palaeoecology and
4 climate studies. Previous research has raised concerns over the possible chemical
5 alteration of microscopic ($< 100 \mu\text{m}$) volcanic glass shards through standard
6 extraction procedures, such as the widely-used acid digestion method. This study
7 subjects ten samples of well-characterised volcanic glasses ranging from basalt to
8 rhyolite to three common methods used in the extraction of volcanic material from
9 lake sediments and peats. The major element geochemistry of each sample was
10 analysed and compared to a control group. The results of this test indicate that
11 basaltic and andesitic glasses are highly susceptible to chemical alteration,
12 particularly to the concentrated corrosive materials used in acid and base digestion
13 techniques. PERMANOVA analysis of the variation within groups suggests that the
14 oxides most susceptible to variation are alkalis from groups I and II (K_2O , Na_2O , CaO ,
15 MgO) and SiO_2 , and the most stable oxides are Al_2O_3 and FeO . Felsic glasses are
16 considerably less susceptible to alteration by both acidic (HCl , HNO_3 , H_2SO_4) and
17 alkaline (KOH) digestions. Our findings have important implications for interpreting
18 the geochemistry of volcanic glasses.

19

20 **1 Introduction**

21 The reliable and non-destructive extraction of tephra is essential for modern
22 applications of tephrochronology and volcanology (Lowe, 2011; Watson et al. 2015).
23 While many methods have been proposed and practiced for the separation of tephra
24 from peat and lake sediments (Hall & Pilcher, 2002; Blockley et al. 2005; Newton et

1 al. 2005), doubts have been raised concerning the geochemical alteration of volcanic
2 glass through these processes. In particular, the use of acid digestion methods has
3 been indicated in the formation of alteration zones around small glass shards,
4 resulting in complications when performing scanning electron microscopy (SEM) or
5 electron probe microanalysis (EPMA) (Blockey et al. 2005). These effects are notably
6 more pronounced in the case of smaller glass shards, producing significant
7 difficulties in the field of tephrochronology where the use of cryptotephra (studies
8 utilising glass shards < 150 µm) is becoming increasingly common for the dating and
9 correlation of sediment and volcanic successions (Watson et al. 2016). Attempts
10 have been made to challenge these claims (Roland et al. 2015); however, this initial
11 case study focused purely on rhyolitic tephra (silica-rich distal deposits of Hekla 4),
12 which comprises slightly more than 75% of the cryptotephra compositions found in
13 western Europe (Swindles et al. 2011; Swindles et al. 2017), and acknowledged that
14 further work on a greater range of glass compositions was required. The ability to
15 accurately compile geochemical profiles of tephra shards is crucial in the
16 identification and correlation of tephra layers to produce isochrons within sediment
17 columns; glass alteration introduces an element of uncertainty which may
18 compromise the reliability of analytical results and their interpretations (Roland et
19 al. 2015; Watson et al. 2016). Several attempts have been made to introduce less
20 chemically destructive techniques, most notably the density separation technique of
21 Blockey et al. (2005). However, the effectiveness of these techniques in removing
22 unwanted biogenic and organic material, such as plant detritus, peat, and biogenic
23 silica, is variable in comparison to traditional chemical digestion-based methods
24 (Brewer et al., 2008; Roland et al., 2015). Therefore, while the original chemical

1 composition of individual shards may be better preserved through density
2 separation techniques, imaging and spectral analysis of samples may still be
3 impaired by low shard recovery rates produced by repeated separation procedures
4 (Roland et al., 2015). This trade-off between shard concentration and geochemical
5 purity of the glass is the cause of dispute, all the more so as the differing methods
6 have not been thoroughly and comprehensively tested against each other.

7

8 Additionally, the apparent preferential preservation of rhyolitic over basaltic tephra
9 in European lake and peatland sites has previously been highlighted by several
10 studies (Wastegård & Davies, 2009; Lawson et al. 2012; Watson et al. 2017). Despite
11 the high frequency of mafic volcanic activity in Iceland (the primary source of
12 European distal tephra deposits (Lawson et al. 2012)), < 3 % of tephtras found in
13 western European sites have a basaltic composition (Swindles et al. 2017). Similar
14 distributions of distal tephra are found in other regions globally – a study of tephra
15 found in several Japanese marine cores found that > 80 % of tephra layers contained
16 > 65 % silica (dacites/rhyolites) (Schindlbeck et al. 2018), and of the 3171 tephtras
17 reported from the Kamchatsky Peninsula (Far-East Russia; Ponomareva et al. (2017)),
18 only 30% contained < 65 % silica (basalts, andesites and dacites). Several possible
19 explanations have been proposed for this discrepancy – firstly, that basaltic material
20 is often a product of less explosive volcanism, resulting in less widespread
21 distribution (Dugmore et al. 1995); secondly, that the higher density of basaltic
22 tephra shards causes them to deposit as fallout more rapidly than rhyolitic shards,
23 resulting in lower concentrations of mafic material at greater distances (Stevenson et
24 al. 2015); and thirdly, that basaltic glass is more susceptible to alteration and

1 hydration processes in acidic environments, such as those found in peatland or
2 produced during traditional sample preparation techniques (Pollard et al. 2003;
3 Blockley et al. 2005). As the historical tephra record in Europe is relatively well-
4 documented (Swindles, 2011; Lawson et al. 2012), many recent studies have focused
5 on extending the tephra record into older sequences, including tephtras from the
6 early Holocene and Younger Dryas periods (Swindles et al. 2017). If the latter
7 hypothesis is correct, many older tephtras, particularly those with a more mafic
8 geochemistry, are likely to be more significantly altered from their initial
9 composition.

10

11 Here, we examine the latter hypothesis by testing the effects of a range of
12 preparation techniques on the geochemistry and morphology of tephtra samples
13 ranging in composition from basaltic to rhyolitic, in order to address the
14 uncertainties presented in many previous tephtra studies. We test the hypothesis
15 that mafic glasses are less robust than felsic glasses when exposed to concentrated
16 acidic and alkaline conditions.

17

18 **2 Materials and Methods**

19 **2.1 Tephtra samples**

20 Each analytical method was performed on ten samples of volcanic glass. Seven of the
21 samples are examples of Icelandic glass commonly found in distal deposits across
22 northern Europe, collected from type site exposures in Iceland. Two are proximal
23 deposits collected from lakes near the edifice of Hekla volcano in southern Iceland,
24 and one is a sample of rhyolite obsidian (glass) from the island of Lipari – part of the

1 Aeolian volcanic arc in the Tyrrhenian Sea. Details of each sample can be found in
2 table 1. The silica content of the samples ranges from 47.6 to 75.1 %, and the
3 average size of the shards chosen for EPMA analysis was similar to the common grain
4 sizes of natural samples (~120 - 150 μm). The samples were chosen according to two
5 broad criteria: while some were chosen due to the frequency of their appearance in
6 European (particularly British and Irish) sediments (e.g. Hekla 1947, Hekla-Selsund),
7 the majority were chosen in order to provide a broad range of chemical
8 compositions for comparison. The sample of Lipari obsidian was chosen for inclusion
9 due to its geochemical homogeneity (the sample is extremely low in magnetite and
10 pyroxene inclusions) and comparative resistance to alteration (Hunt & Hill, 1996),
11 while others, such as RL1 and Hekla-Selsund Phase 1, were chosen for their chemical
12 heterogeneity, under the assumption that if one compositional group were
13 preferentially affected by a given treatment, it would be possible to show this within
14 a single sample.

15

16 [Insert Table 1: A summary of the tephra samples used for analysis]

17

18 **2.2 Processing methods**

19 **2.2.1 Control (No treatment)**

20 Samples in the control group were not subjected to any chemical treatment
21 following the combination of the glass with peat. Samples were washed through a 16
22 μm sieve with deionised water and then dried at 105 $^{\circ}\text{C}$ prior to electron probe
23 analysis. While density separation techniques are becoming a common procedure in
24 the field of tephrochronology, none were performed at any stage in this study as the

1 process is rarely used in combination with acid or base treatments (Blockley et al.,
2 2005).

3

4 **2.2.2 Muffle furnace burning and dilute hydrochloric acid (Method 1)**

5 Following the tephra extraction methods of Hall & Pilcher (2002) and Swindles et al.
6 (2010), the samples subjected to this method were dried overnight at 105 °C, and
7 then burnt in a muffle furnace at 600 °C for six hours. The resulting ashes were then
8 transferred to 15 ml centrifuge tubes, and suspended in 3 ml of 1M hydrochloric acid
9 (HCl) for 24 hours. The tubes were then topped up to 14.5 ml with deionised water,
10 and centrifuged at 3000 rpm for 10 minutes to concentrate the tephra at the base of
11 the tubes. The remaining acid was then removed by washing the samples through a
12 16 µm sieve with deionised water. While there is some suggestion that the use of
13 the muffle furnace may not be suitable when preparing glass shards for EPMA (Hall
14 & Pilcher, 2002), the method is still commonly used for this purpose (Hang et al,
15 2006; Swindles, 2010; Watson et al, 2016).

16

17 **2.2.3 Acid digestion (Method 2)**

18 This method follows the modified procedure of Persson (1971), published on
19 'TephraBase' (http://www.tephrabase.org/tephra_dig.html), where a detailed
20 methodology may be found. The method is also used by Dugmore et al. (1992) and
21 Swindles et al. (2010) and is thought to be most effective in removing organic-rich,
22 ombrotrophic peat sediments (Roland et al. 2015), though it is also used in
23 minerogenic lake samples (Renberg et al., 2002).

1 The wet samples were placed into 500 ml beakers, and 100 ml of 98 % sulfuric acid
2 (H_2SO_4) was added to cover the samples. The hotplate was then switched on, and
3 turned to maximum ($\sim 300\text{ }^\circ\text{C}$). Once the initial boiling had subsided (approximately
4 5 minutes), the samples were left to react for 90 minutes. 10 ml of 68-72% HNO_3
5 (Standard Laboratory Reagent) was then slowly added, and the contents of the flasks
6 left to simmer for a further 1 hr until the solution became pale yellow or colourless.
7 The hotplate was then switched off, and the samples left to cool to room
8 temperature (approximately 45 minutes). Following this step, 400 ml of distilled
9 water was slowly added until no further vapours were released from the beakers.
10 The samples were then thoroughly washed through a $16\text{ }\mu\text{m}$ sieve, centrifuged at
11 3000 rpm for 10 minutes, and the supernatant pipetted off.

12

13 **2.2.4 Acid/base digestion (Method 3)**

14 The third method replicated the procedure utilised by Watson et al. (2016) and
15 Matthews-Bird et al. (2017). In the instances described by those studies, the method
16 was used to prepare the samples for radiocarbon analysis.

17 The samples in this study were placed in 500 ml beakers with 150 ml of 1M HCl, and
18 heated to 80°C for 2 hours. The samples were then cooled to room temperature over
19 the course of 30 minutes and rinsed with deionised water, before being transferred
20 to clean beakers. 150 ml of 0.5M KOH was then added, and the samples were again
21 heated to $80\text{ }^\circ\text{C}$ for 2 hours. Following this, 10-30 ml of deionised water was added in
22 small increments until no further material was extracted, and the mixtures were
23 then cooled to room temperature as before, and rinsed through a $10\text{ }\mu\text{m}$ mesh with
24 500 ml of deionised water before being returned to their beakers. A further 150 ml

1 of 1M HCl was then added to the samples, which were then heated again to 80°C for
2 5 hours. The samples were then cooled and rinsed, washed through a 16 µm sieve,
3 centrifuged at 3000 rpm for 10 minutes, and the supernatant pipetted off.

4

5 **2.3 Electron Probe Microanalysis**

6 The samples were dried and mounted on 25.5 mm disks in Epo-Tek® resin, and
7 finished with a 0.25 µm diamond polish to ensure exposure and a polished surface.

8 EPMA was performed at the Tephra Analysis Unit at the University of Edinburgh,
9 using the “combined analysis method” described in detail in Hayward (2012). All

10 analyses were performed using a 5 µm diameter beam of 15 kV, varying only the

11 current between 2 nA for Na, Mg, Al, Si, K, Ca, and Fe quantities, and 80 nA for Ti and

12 Mn. Secondary (external) glass standards (basalt BCR-2G and Lipari rhyolite) were

13 analysed before each EPMA run, and a PAP correction applied. Analyses were

14 performed as close to the centre of each shard (i.e. the centre point of the x and y

15 axes) as possible in order to ensure accurate geochemical profiling of the glass, in

16 accordance with standard laboratory procedures. Shards that were not sufficiently

17 exposed across the polished surface were excluded.

18

19 **2.4 Statistical Analysis – PERMANOVA**

20 PERMANOVA is a non-parametric multivariate method of statistical analysis.

21 Originally developed as an adaptation of traditional MANOVA methods (Anderson,

22 2001; McArdle & Anderson, 2005) to better suit the non-normal distributions and

23 discrete (rather than continuous) data values found in ecological datasets (while

24 ecological datasets were the intended target, the developers stated that the method

1 was likely to be applicable across the natural sciences; Anderson, 2001),
2 PERMANOVA is most applicable when handling datasets with asymmetric
3 distributions, and in variables containing multiple zeros. It is therefore useful in the
4 comparison of diverse geochemical profiles, in which element distributions are
5 unlikely to follow a pattern of normal distribution.

6 The EPMA data were normalised to 100 % (i.e. to an anhydrous basis) prior to
7 multivariate analysis in order to ensure authentic comparison between datasets
8 (WoldeGabriel et al., 2005; Pearce et al., 2007).

9

10 **3 Results**

11 **3.1 Notes on removal of organic material**

12 While both the acid digestion (method 2) and burning/dilute acid (method 1)
13 processes were effective in removing unwanted organic materials from the sample,
14 the process of acid digestion was by far the most thorough in removing the peat, if
15 slightly less time efficient when preparing large batches of samples. However,
16 following method 3, small amounts of organic material remained within the sample,
17 and were visible under an optical microscope. These contaminants were identified as
18 bleached moss and plant material. The organic material was not of a sufficient
19 quantity to obstruct microscope analysis.

20

21 **3.2 Glass Alteration**

22 **3.2.1 Glass Morphology**

23 Through optical and SEM imagery, a clear difference between the glass
24 morphologies of shards subjected to each treatment can be seen. Alteration rims of

1 between 15-75 μm are immediately visible in most shards subjected to acid
2 digestion (method 2), with most samples displaying a zone of glassy, crystal-rich
3 (typically quartz- and feldspar-rich) material (see figure 1). Alteration rims are also
4 frequently seen in shards subjected to treatment method 1, though they are
5 typically smaller in diameter, between 15-40 μm . However, the most significant
6 changes in shard morphology can be observed following base (KOH) digestion; many
7 shards subjected to this treatment appear substantially degraded, sometimes taking
8 on a pseudo-dendritic appearance (see figure 1 (d)). In the cases of more crystal-rich
9 tephra, the glassy matrix appears to be preferentially dissolved, leaving the
10 plagioclase crystals relatively unaffected (see figure 1 (b. iv.)). Unlike in the acid
11 treatments, these shards do not exhibit a well-defined zone of alteration, with few
12 exceptions.

13

14 [Insert Figure 1: SEM images of volcanic glass belonging to a) Katla 1357; b) Hekla
15 1991; c) Lipari glass; and analysed following chemical treatments: i) Control group; ii)
16 Acid digestion; iii) Burning + dilute HCl; iv) Base digestion. Red arrows indicate zones
17 of alteration. Image d) shows a pattern of corrosion produced by base digestion on a
18 shard of Hekla 1341 glass. Image a) iv. is an optical image – all useful shards of Katla
19 1357 were considerably degraded through base digestion, and were not clearly
20 visible through SEM imagery.]

21

22 The evidence gathered in this study strongly indicates that underlying glass
23 geochemistry plays a role in the degree of shard alteration. Shards from the basaltic
24 Katla 1357 (K1357) eruption (average $\text{SiO}_2 \sim 48 \text{ wt } \%$; figure 1 (a)) show notably

1 greater morphological changes as a result of each treatment than those shards with
2 a higher silica content, such as the andesitic Hekla 1991 (average SiO₂ content 56.48
3 %; figure 1 (b)), or the rhyolitic Lipari obsidian (SiO₂ ~75 wt %; figure 1 (c)). The
4 dissolution of the K1357 shards following base digestion (method 3) was sufficiently
5 extensive to entirely prohibit the use of EPMA in that sample, while the Lipari
6 obsidian was unusual in that it exhibited no alteration rim following weak or
7 concentrated acid treatment, and only a narrow rim of 5-8 μm following base
8 digestion.

9

10 **3.2.2 Geochemistry**

11 [insert Figure 2: Selected TAS diagrams showing group variations in geochemical
12 classifications following chemical treatments of volcanic glass. Purple circles –
13 control group; red diamonds – burning + dilute HCl; green squares – acid digestion;
14 yellow stars – base digestion. These examples were selected for the clarity of
15 variation from the untreated group across a range of SiO₂ contents. Sample RL1 has
16 been included to variation across initial composition within a single sample. TAS
17 classification after Le Bas et al., 1986.]

18

19 Our results show a large amount of variability in glass geochemistry following
20 chemical treatment. While many oxide concentrations show significant variation
21 across treatments (discussed further in section 3.3), the most consistently significant
22 differences, both positive and negative, occur in the concentrations of Na₂O, CaO,
23 K₂O, MgO, and SiO₂. While mean relative concentrations of Na₂O and K₂O typically
24 decrease following chemical treatment of the glasses, the relative concentrations of

1 SiO₂, MgO, and CaO typically increase. Additionally, there is a clear and persistent
2 trend across almost all major element oxides wherein variation compared to the
3 control group is greater following acid and base digestions (methods 2 and 3) than
4 those subjected to method 1. The four exceptions to this trend are: the Lipari glass,
5 which displays very few variations in mean oxide concentration to a statistically
6 significant level (5%) of any major element under any tested conditions (the
7 exception being method 2, which produced a 5.52% increase in mean FeO content);
8 and the SL1, RL1, and Hekla 1991 samples, in which the initial geochemistry was
9 found to be variable. In these cases, significant statistical deviations from the control
10 group may simply be a result of variability within the natural glass shard population.
11 A full summary of major element geochemistry and secondary samples can be found
12 in appendix 1.

13

14 [Insert Figure 3: Boxplots and ternary diagrams displaying variations in major
15 element geochemistry for a) Katla 1357; b) Hekla 1947; c) Lipari glass. Symbols are
16 coloured as follows: purple – control group; red – burning + HCl; green – acid
17 digestion; yellow – base digestion.]

18

19 In addition to the trend described above, we also find a correlation in responses to
20 chemical treatment with initial SiO₂ abundances (i.e. the composition of the control
21 group). The examples shown in figure 3 summarise the geochemical alterations to a
22 basalt, andesite, and rhyolite respectively. In the basaltic K1357 sample (average
23 initial SiO₂ = 47.6 wt %), the mean Na₂O content varies negatively by 61.7 %
24 following acid digestion (method 2) when compared to the control group. In the

1 andesitic Hekla 1947 (average initial $\text{SiO}_2 = 61.5$ wt %), the Na_2O concentration
2 decreases between the control and acid digestion treatment by 5.7 %, and in the
3 rhyolitic Lipari glass ($\text{SiO}_2 = 75.1$ wt %) the decrease in the mean concentration is as
4 low as 0.667 %. Following base digestion (method 3), the Na_2O content deviates
5 negatively from the control group by 26 % for Katla 1357, 38.2 % for Hekla 1947, and
6 0.48 % for Lipari glass. Both the basalt and the andesite display significantly more
7 variation across groups when compared with the rhyolite.

8

9 Certain samples appear to display a trend of 'homogenisation' in the range of
10 observed compositions following chemical treatment. For example, the control
11 groups of Hekla 1341 and Hekla 1991 glass both have a higher range of Si/TA (total
12 alkali) values than in the subsequent treatment groups, particularly those subjected
13 to methods 2 and 3, reflecting an apparent loss of alkali oxides. The affected
14 composition ranges typically occur below ~ 55 SiO_2 wt% and TA 4-5 wt%. In these
15 instances, the chemical composition of the glasses apparently 'removed' by
16 concentrated chemical treatment are also relatively low in wt %s of network forming
17 cations other than Si. Taking one example of 'removed' material in the Hekla 1341
18 basalts, TiO_2 (Ti^{4+}) constitutes < 4 wt% and Al_2O_3 (Al^{3+}) < 15 wt% . Likewise, TiO_2
19 comprises < 0.25 wt% and Al_2O_3 < 13 wt% in the Hekla 1991 basalts. The NBO/T ratio
20 of these glasses (a measure of polymerisation; calculated after Mysen et al., 1985),
21 which are not present in the samples subjected to concentrated acid treatment, is
22 subsequently higher than that of the average group composition (Hekla 1341 basalts
23 $\text{NBO/T} = 2.96$ (average 1.77); Hekla 1991 basalts $\text{NBO/T} = 3.22$ (average 2.28)). The
24 lower polymerisation of these glasses would substantially increase their solubility,

1 which may explain their apparent absence in the samples following concentrated
2 solution treatments.

3

4 **3.2.3 PERMANOVA**

5 Table 2 shows the results of the PERMANOVA analysis of each method in comparison
6 to the oxide quantities measured in the control group. In this instance we regard a *P*
7 value of < 0.01 (1 %) to be statistically significant, i.e. indicating that the wt% of that
8 element has changed to a significant degree. Our results confirm that the most
9 consistently variable oxide is K₂O, which shows a significant within-group variation in
10 8 out of 30 analyses. CaO and SiO₂ both show significant within-group variation in 7
11 of 30 analyses, and Na₂O, MgO, MnO, and TiO₂ each show significant variation in 5 of
12 30. Additionally, samples which show significant variation in at least one oxide across
13 all three chemical treatments show fewer variations, and less significant variance
14 (lower *F* values), in the method 1 treatment group than in either the acid or base
15 digestion groups (methods 2 and 3).

16

17 The PERMANOVA analysis also allows comparison between sample groups. For
18 example, while the Hekla-Selsund Phase 2 sample (average SiO₂ content 53.6 %)
19 shows four statistically significant variations in major element oxide concentrations
20 (K₂O, CaO, SiO₂, and TiO₂) following methods 2 and 3, and two following method 1
21 (TiO₂ and MnO), the Lipari glass samples do not show statistically significant
22 variations in any oxide following any treatment. Comparison of samples with
23 contrasting SiO₂ content (see table 3), reveals a broad pattern of lower susceptibility
24 to chemical alteration with increasing silica content.

1

2 [Insert Table 2: PERMANOVA results]

3

4 [Insert Table 3: Summary of variations in relative oxide concentration against
5 average SiO₂ content in control group, NBO/T, and H₂O by difference. Statistically
6 significant ($P < 0.01$) variations are highlighted in bold. As comparisons are drawn
7 between normalised results, constant sum effects should be taken into account.]

8

9 **4 Discussion**

10 This study confirms persistent assertions within tephrochronology that substantial
11 chemical alteration of volcanic glass via commonly used extraction techniques,
12 namely the acid digestion method, is possible, particularly for basaltic and low-silica
13 andesitic tephra (< ~60% SiO₂; Blockley et al, 2005). The assertion of Roland et al.
14 (2015) that no significant geochemical variation could be found following acid
15 digestion is supported by our findings, as the felsic samples (> 63% SiO₂) in our study
16 were among the least susceptible to geochemical alteration. In particular, the highly
17 silicic Lipari glasses were by far the least prone to any chemical perturbation. While
18 the precise mechanisms behind this relationship require further study, we suggest
19 that the increased polymerisation of silica chains in rhyolitic glass may provide a
20 stabilising factor, preventing the leaching of mobile elements (Iler, 1979; Chan, 1989;
21 Dultz et al, 2016). Furthermore, while outside the scope of the data presented in this
22 study, it is likely that volatile content of the tephra could affect the susceptibility of
23 the glasses to alteration, as the formation of molecules such as OH⁻ and CO₃²⁻ (for
24 example) reduce the degree of glass polymerisation.

1

2 Additionally, concern has previously been raised over the apparent
3 underrepresentation of basaltic glasses in the European tephra record, compared to
4 the more felsic (evolved) rock varieties sourced from Icelandic (Lawson et al. 2012;
5 Watson et al. 2016; Watson et al. 2017). While basaltic glass is not entirely absent
6 from European peatland and lake records, our results give weight to the theory that
7 this apparent bias may be due in part to either partial alteration or complete
8 destruction of basaltic material during glass shard extraction, as suggested by
9 Watson et al. (2017). Furthermore, it is possible that the acidic conditions present in
10 peat bogs (typically pH 3-4; Sanger et al. 1993; Klavins & Purmalis, 2013) may play a
11 role in creating the apparent bias in the record; a long residence time in such
12 conditions may cause alteration or dissolution of a significant percentage of basaltic
13 shards in a given deposit.

14

15 Also of note is the apparently consistent creation in some samples of novel glass
16 geochemistry – in other words, instances in which the combined variation in one or
17 more major element weight percentages is significant enough to place multiple glass
18 shards in new geochemical category when plotting against standard TAS definitions.
19 This is especially relevant for studies concerning cryptotephra < 30-50 µm in
20 diameter (frequently encountered in distal tephra studies; Lowe et al., 2011; Pearce
21 et al., 2014), or those with a high surface area-to-volume ratio, such as tricusate
22 shards or those with multiple bubble walls, as any alteration in those instances is
23 likely to affect a greater percentage of the glass composition in those shards.
24 Particularly important are those compositions which transition from sub-alkaline to

1 alkaline fields. These alkaline compositions are only rarely erupted in Iceland (Wood,
2 1978; Nicholson et al. 1991; Gudmundsdóttir et al. 2018), yet are occasionally
3 reported in European cryptotephra studies which variably attribute the material to
4 Icelandic eruptions or suggest ultradistal sources, such as the Cascade Range or
5 Alaskan volcanoes of North America (Jensen et al., 2014; van der Bilt et al., 2017;
6 Plunkett & Pilcher, 2018). Figure 4 shows a composite TAS diagram combining
7 several reported Icelandic cryptotephra, overlain with selected anomalous results
8 from this study. While some analyses are clearly distinguishable from the wider
9 trend of Icelandic geochemistry, many of the variations produced by all three
10 treatment methods fall well within the boundaries of reported Icelandic
11 trachyandesites in the European tephra record. Although it is possible that these
12 reported analyses represent the original geochemistry of the tephra shard in
13 question, the control groups for each of the anomalous trachyandesites and
14 trachytes found in this study did not fall into either geochemical category. It is
15 therefore also possible that some reported trachyandesites may have been
16 unintentionally manufactured as a result of chemical alteration during extraction.
17 Great care should therefore be taken in the interpretation of apparently ultra-distal
18 tephras, particularly regarding the relative contents of groups I and II oxides (K_2O ,
19 Na_2O , CaO , MgO), which we find to be particularly susceptible to alteration. It is
20 however possible that this same susceptibility may have applications in assessing the
21 validity of volcanic glass datasets, although the exact nature of any potential
22 statistical test based on that data is beyond the scope of this study.
23

1 [Insert Figure 4. Composite TAS diagram showing the range of reported Icelandic
2 geochemistry against geochemical variations produced by chemical extraction in this
3 study. This study: green squares – acid digestion; orange diamonds – burning + HCl;
4 yellow stars – base digestion. Existing literature is denoted with circle symbols. Grey
5 – Plunkett & Pilcher (2018) (assigned 'Icelandic'). Red – Plunkett & Pilcher (2018)
6 (assigned 'non-Icelandic'). Purple – Pilcher et al. (2005) (selected Borge tephtras).
7 Blue – composite Icelandic data from Mangerud et al. (1984); Mangerud, Furnes &
8 Johansen (1986); Pilcher, Hall & McCormac (1996); Boygle (1994); Dugmore et al.
9 (1992); Dugmore, Larsen & Newton (1995); Dugmore & Newton (1997), Larsen,
10 Dugmore et al. (1999); Wastegard et al. (2001); Hall & Pilcher (2002); Chambers et al.
11 (2004); Swindles (2006); Davies et al. (2007); Rea, Swindles & Roe (2012); Ratcliffe et
12 al. (2017). Cyan – composite Katla data from Boygle (1994); Streeter & Dugmore
13 (2014).]

14

15 The findings of this experiment ultimately suggest that the vulnerability of mafic
16 tephra and cryptotephra to geochemical alteration by laboratory techniques may be
17 greater than previously thought. As basaltic tephra is favoured over more
18 magmatically evolved material in many petrogenetic studies, the preservation of
19 these tephtras in a laboratory setting is increasingly important. Therefore, while non-
20 destructive methods of glass extraction are often more time-consuming and labour-
21 intensive than chemical methods, it may be of greater benefit to future studies to
22 exercise caution and discretion when handling silica-poor glasses, particularly those
23 with a small surface area/perimeter ratio.

24

1 **5 Conclusions**

2 [1] The use of burning & dilute HCl, concentrated H₂SO₄ and HNO₃ (as used in the
3 common acid digestion method of tephra preparation), and concentrated KOH in the
4 extraction of volcanic glass are all sufficient to cause statistically significant variations
5 in the less stable element oxides;

6 [2] The oxides most susceptible to variation are K₂O, CaO, SiO₂, and Na₂O. The most
7 statistically stable oxides are Al₂O₃ and FeO.

8 [3] Basaltic and basaltic andesitic glasses are most susceptible to alteration through
9 exposure to concentrated acidic (HNO₃, H₂SO₄) and basic (KOH) conditions;

10 [4] Concentrated acids and bases also cause the destruction of perimeter glass
11 material in volcanic glass, particularly glasses of a mafic composition;

12 [5] These systematic alterations of volcanic glass may have implications for
13 previously published studies of tephra geochemistry and stratigraphy.

14

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1

2 References

- 3 1. Anderson, M.J. (2001) A new method for non-parametric multivariate analysis of variance.
4 Austral Ecology, 26: 32-46.
- 5 2. Blockley, S.P.E., et al. (2005) A new and less destructive laboratory procedure for the physical
6 separation of distal glass tephra shards from sediments. *Quaternary Science Reviews*, 24(16-
7 17), pp.1952-1960.
- 8 3. Boyle, J.E. (1994) *Tephra in lake sediments: An unambiguous geochronological marker?*
9 PhD. Thesis, University of Edinburgh, Edinburgh
- 10 4. Brewer, T. S., Leng, M. J., Mackay, A. W., Lamb, A. L., Tyler, J. J., & Marsh, N. G. (2008).
11 Unravelling contamination signals in biogenic silica oxygen isotope composition: the role of
12 major and trace element geochemistry. *Journal of Quaternary Science: Published for the*
13 *Quaternary Research Association*, 23(4), 321-330.
- 14 5. Chambers, F.M., et al. (2004) Tephrostratigraphy of An Loch Mór, Inis Oírr, western Ireland:
15 implications for Holocene tephrochronology in the northeastern Atlantic region. *Holocene*
16 14, 703-720.
- 17 6. Chan, S. H. (1989). A review on solubility and polymerization of silica. *Geothermics*, 18(1-2),
18 49-56.
- 19 7. Davies, S.M., et al. (2007) Cryptotephra sedimentation processes within two lacustrine
20 sequences from west central Sweden. *Holocene* 17, 319-330.
- 21 8. Dugmore, A.J., et al. (1992) Geochemical stability of fine-grained silicic tephra layers in
22 Iceland and Scotland. *Journal of Quaternary Science* 7, 173-183.
- 23 9. Dugmore, A.J., Larsen, G.R. and Newton, A.J., (1995) Seven tephra isochrones in
24 Scotland. *The Holocene*, 5(3), pp.257-266.
- 25 10. Dugmore, A.J. and Newton, A.J. (1997) Holocene tephra layers in the Faroe Islands.
26 *Frodskaparrit* 45, 141-154.
- 27 11. Dultz, S., Behrens, H., Hensch, G., & Deubener, J. (2016). Electrolyte effects on surface
28 chemistry of basaltic glass in the initial stages of dissolution. *Chemical Geology*, 426, 71-84.
- 29 12. Einarsson, E. H., Larsen, G., & Thorarinsson, S. (1980). The Sólheimar tephra layer and the
30 Katla eruption of 1357. *Náttúrufræðistofnun Íslands*
- 31 13. Global Volcanism Program (2013) Hekla (372070) in *Volcanoes of the World*, v. 4.7.6. Venzke,
32 E (ed.). Smithsonian Institution. Downloaded 18 Mar 2019
33 (<https://volcano.si.edu/volcano.cfm?vn=372070>). [https://doi.org/10.5479/si.GVP.VOTW4-](https://doi.org/10.5479/si.GVP.VOTW4-2013)
34 2013
- 35 14. Gudmundsdóttir, E. R., Schomacker, A., Brynjólfsson, S., Ingólfsson, Ó., & Larsen, N. K. (2018).
36 Holocene tephrostratigraphy in Vestfirðir, NW Iceland. *Journal of Quaternary Science*, 33(7),
37 827-839.
- 38 15. Gudmundsson, A., et al. (1992). The 1991 eruption of Hekla, Iceland. *Bulletin of Volcanology*,
39 54(3), 238-246.
- 40 16. Hall, V.A. and Pilcher, J.R. 2002. Late-Quaternary Icelandic tephtras in Ireland and Great
41 Britain: detection, characterization and usefulness. *Holocene*, 12, pp. 223-230
- 42 17. Hallam, B. R., Warren, S. E., & Renfrew, C. (1976, December). Obsidian in the western
43 Mediterranean: characterisation by neutron activation analysis and optical emission
44 spectroscopy. In *Proceedings of the Prehistoric Society* (Vol. 42, pp. 85-110). Cambridge
45 University Press.
- 46 18. Hang, T., Wastegård, S., Veski, S., & Heinsalu, A. (2006). First discovery of cryptotephra in
47 Holocene peat deposits of Estonia, eastern Baltic. *Boreas*, 35(4), 644-649.
- 48 19. Hayward, C., (2012) High spatial resolution electron probe microanalysis of tephtras and melt
49 inclusions without beam-induced chemical modification. *The Holocene*, 22(1), pp.119-125.
- 50 20. Hunt, J. B., & Hill, P. G. (1996). An inter-laboratory comparison of the electron probe
51 microanalysis of glass geochemistry. *Quaternary International*, 34, 229-241.
- 52 21. Iler, Ralph K. (1979). *Chemistry of Silica - Solubility, Polymerization, Colloid and Surface*
53 *Properties and Biochemistry*. John Wiley & Sons.

- 1 22. Jensen, B. J. L., Mackay, H., Pyne-O'Donnell, S., Plunkett, G., Hughes, P. D. M., Froese, D. G., &
2 Booth, R. (2014, December). Exceptionally long distance transport of volcanic ash:
3 implications for stratigraphy, hazards and the sourcing of distal tephra deposits. In AGU Fall
4 Meeting Abstracts.
- 5 23. Klavins, M., & Purmalis, O. (2013). Properties and structure of raised bog peat humic acids.
6 *Journal of Molecular Structure*, 1050, 103-113.
- 7 24. Larsen, G., Dugmore, A., J. and Newton, A.J. (1999) Geochemistry of historic silicic tephra in
8 Iceland. *The Holocene* 9(4), 463-471
- 9 25. Larsen, G., Newton, A. J., Dugmore, A. J., & Vilmundardóttir, E. G. (2001). Geochemistry,
10 dispersal, volumes and chronology of Holocene silicic tephra layers from the Katla volcanic
11 system, Iceland. *Journal of Quaternary Science: Published for the Quaternary Research*
12 *Association*, 16(2), 119-132.
- 13 26. Lawson, I.T., Swindles, G.T., Plunkett, G. and Greenberg, D., (2012) The spatial distribution of
14 Holocene cryptotephra in north-west Europe since 7 ka: implications for understanding ash
15 fall events from Icelandic eruptions. *Quaternary Science Reviews*, 41, pp.57-66.
- 16 27. Le Bas, M. L., Maitre, R. L., Streckeisen, A., Zanettin, B., & IUGS Subcommittee on the
17 Systematics of Igneous Rocks. (1986). A chemical classification of volcanic rocks based on the
18 total alkali-silica diagram. *Journal of petrology*, 27(3), 745-750.
- 19 28. Lowe, D.J. (2011). Tephrochronology and its application: a review. *Quaternary*
20 *Geochronology*, 6(2), 107-153
- 21 29. Mangerud, J., Furnes, H., and Johansen, J. (1986) A 9,000 year old ash bed on the Faroe
22 Islands. *Quaternary Research* 26, 262-265.
- 23 30. Mangerud, J., et al. (1984) A Younger Dryas ash bed in western Norway and its possible
24 correlations with tephra in cores from the Norwegian Sea and the North Atlantic. *Quaternary*
25 *Research* 21, 85-104.
- 26 31. Matthews-Bird, et al. (2017) Aquatic community response to volcanic eruptions on the
27 Ecuadorian Andean flank: evidence from the palaeoecological record. *Journal of*
28 *Paleolimnology*, 58(4), pp.437-453.
- 29 32. McArdle, B.H. & Anderson, M.J. (2001) Fitting multivariate models to community data: a
30 comment on distancebased redundancy analysis. *Ecology*, 82, 290-297.
- 31 33. Mysen, B. O., Virgo, D., & Seifert, F. A. (1985). Relationships between properties and
32 structure of aluminosilicate melts. *American Mineralogist*, 70(1-2), 88-105.
- 33 34. Newton, A.J., Dugmore, A.J. and Gittings, B.M., (2007) TephraBase: tephrochronology and
34 the development of a centralised European database. *Journal of Quaternary Science*, 22(7),
35 pp.737-743.
- 36 35. Nicholson, H. et al. (1991) Geochemical and Isotopic Evidence for Crustal Assimilation
37 Beneath Krafla, Iceland, *Journal of Petrology*, 32(5), pp. 1005–1020, [https://doi-](https://doi-org.wam.leeds.ac.uk/10.1093/petrology/32.5.1005)
38 [org.wam.leeds.ac.uk/10.1093/petrology/32.5.1005](https://doi-org.wam.leeds.ac.uk/10.1093/petrology/32.5.1005)
- 39 36. Pearce, N. J., Denton, J. S., Perkins, W. T., Westgate, J. A., & Alloway, B. V. (2007). Correlation
40 and characterisation of individual glass shards from tephra deposits using trace element laser
41 ablation ICP-MS analyses: current status and future potential. *Journal of Quaternary Science*,
42 22(7), 721-736.
- 43 37. Pearce, N. J., Abbott, P. M., & Martin-Jones, C. (2014). Microbeam methods for the analysis
44 of glass in fine-grained tephra deposits: a SMART perspective on current and future trends.
45 *Geological Society, London, Special Publications*, 398(1), 29-46.
- 46 38. Persson, C., 1971. *Tephrochronological investigation of peat deposits in Scandinavia and on*
47 *the Faroe Islands*. Sveriges reproduktions AB (distr.).
- 48 39. Pilcher, J.R., Hall, V.A. and McCormac, F.G. (1996) An outline tephrochronology for the
49 Holocene of the north of Ireland. *Journal of Quaternary Science* 11 (6), 485-494.
- 50 40. Plunkett, G., & Pilcher, J. R. (2018). Defining the potential source region of volcanic ash in
51 northwest Europe during the Mid-to Late Holocene. *Earth-Science Reviews*, 179, 20-37.
- 52 41. Pollard, A.M., Blockley, S.P.E. and Ward, K.R., (2003) Chemical alteration of tephra in the
53 depositional environment: theoretical stability modelling. *Journal of Quaternary*
54 *Science*, 18(5), pp.385-394.
- 55 42. Ponomareva, V., Portnyagin, M., Pendea, I. F., Zelenin, E., Bourgeois, J., Pinegina, T., &
56 Kozhurin, A. (2017). A full Holocene tephrochronology for the Kamchatsky Peninsula region:

- 1 Applications from Kamchatka to North America. *Quaternary Science Reviews*, 168, 101-122.
2 doi:10.1016/j.quascirev.2017.04.031
- 3 43. Ratcliffe, J., et al. (2017) Contemporary carbon fluxes do not reflect the long-term carbon
4 balance for an Atlantic blanket bog. *The Holocene*, 28(1)
- 5 44. Rea, HA, Swindles, GT and Roe, HM (2012) The Hekla 1947 tephra in the north of Ireland:
6 regional distribution, concentration and geochemistry. *Journal of Quaternary Science* 27,
7 425-431.
- 8 45. Renberg, I., Brännvall, M. L., Bindler, R., & Emteryd, O. (2002). Stable lead isotopes and lake
9 sediments—a useful combination for the study of atmospheric lead pollution history. *Science*
10 *of the Total Environment*, 292(1-2), 45-54.
- 11 46. Roland, T.P., Mackay, H. and Hughes, P.D.M., (2015). Tephra analysis in ombrotrophic
12 peatlands: a geochemical comparison of acid digestion and density separation
13 techniques. *Journal of Quaternary Science*, 30(1), pp.3-8.
- 14 47. Rose, N.L., Golding, P.N.E. and Battarbee, R.W., (1996) Selective concentration and
15 enumeration of tephra shards from lake sediment cores. *The Holocene*, 6(2), pp.243-246.
- 16 48. Sanger, L. J., Billett, M. F., & Cresser, M. S. (1994). The effects of acidity on carbon fluxes
17 from ombrotrophic peat. *Chemistry and Ecology*, 8(4), 249-264.
- 18 49. Schindlbeck, J. C., Kutterolf, S., Straub, S. M., Andrews, G. D. M., Wang, K., &
19 Mleneck-Vautravers, M. J. (2018). One million years tephra record at IODP sites U1436 and
20 U1437: Insights into explosive volcanism from the Japan and Izu arcs. *Island Arc*, 27(3),
21 e12244-n/a. doi:10.1111/iar.12244
- 22 50. Stevenson, J.A., et al. (2012) Distal deposition of tephra from the Eyjafjallajökull 2010 summit
23 eruption. *Journal of Geophysical Research: Solid Earth*, 117(B9).
- 24 51. Streeter, R. and Dugmore, A. (2014) Late-Holocene land surface change in a coupled social
25 ecological system, southern Iceland: a cross-scale tephrochronology approach. *Quaternary*
26 *Science Reviews* 86, 99-114.
- 27 52. Swindles, G. (2006) Reconstructions of Holocene climate change from peatland in the north
28 of Ireland. Unpublished PhD thesis, Queen's University, Belfast
- 29 53. Swindles, G. T., De Vleeschouwer, F., & Plunkett, G. (2010). Dating peat profiles using tephra:
30 stratigraphy, geochemistry and chronology. *Mires and Peat*, 7.
- 31 54. Swindles, G. T., Lawson, I. T., Savov, I. P., Connor, C. B., & Plunkett, G. (2011). A 7000 yr
32 perspective on volcanic ash clouds affecting northern Europe. *Geology*, 39(9), 887-890.
- 33 55. Swindles, G.T. et al. (2017) Holocene volcanic ash database for Northern Europe. Database.
34 DOI: 10.13140/RG.2.2.11395.60966.
- 35 56. van der Bilt, W. G., Lane, C. S., & Bakke, J. (2017). Ultra-distal Kamchatkan ash on Arctic
36 Svalbard: towards hemispheric cryptotephra correlation. *Quaternary Science Reviews*, 164,
37 230-235.
- 38 57. Wastegård, S., et al. (2001) The Mjauvotn tephra and other Holocene tephra horizons from
39 the Faroe Islands: a link between the Icelandic source region, the Nordic Seas, and the
40 European continent. *The Holocene* 11(1), 101-109.
- 41 58. Wastegård, S., Rundgren, M., Schoning, K., Andersson, S., Björck, S., Borgmark, A., &
42 Possnert, G. (2008). Age, geochemistry and distribution of the mid-Holocene Hekla-
43 S/Kebister tephra. *The Holocene*, 18(4), 539-549.
- 44 59. Wastegård, S. and Davies, S.M., (2009) An overview of distal tephrochronology in northern
45 Europe during the last 1000 years. *Journal of Quaternary Science: Published for the*
46 *Quaternary Research Association*, 24(5), pp.500-512.
- 47 60. Watson, E. J., Swindles, G. T., Lawson, I. T., & Savov, I. P. (2015). Spatial variability of tephra
48 and carbon accumulation in a Holocene peatland. *Quaternary Science Reviews*, 124, 248-
49 264.
- 50 61. Watson, E.J., Swindles, G.T., Lawson, I.T. and Savov, I.P., (2016) Do peatlands or lakes provide
51 the most comprehensive distal tephra records?. *Quaternary Science Reviews*, 139, pp.110-
52 128.
- 53 62. Watson, E.J., Swindles, G.T., Savov, I.P., Lawson, I.T., Connor, C.B. and Wilson, J.A., (2017)
54 Estimating the frequency of volcanic ash clouds over northern Europe. *Earth and Planetary*
55 *Science Letters*, 460, pp.41-49.
- 56 63. WoldeGabriel, G., Hart, W. K., & Heiken, G. (2005). Innovative tephra studies in the East
57 African rift system. *Eos, Transactions American Geophysical Union*, 86(27), 255-255.

64. Wood, D.A. (1978) Major and Trace Element Variations in the Tertiary Lavas of Eastern Iceland and their Significance with respect to the Iceland Geochemical Anomaly, *Journal of Petrology*, 19 (3), pp 393–436, <https://doi.org/10.1093/petrology/19.3.393>

Legends

Table 1: A summary of the tephra samples used for analysis

Figure 1: SEM images of volcanic glass belonging to a) Katla 1357; b) Hekla 1991; c) Lipari glass; and analysed following chemical treatments: i) Control group; ii) Acid digestion; iii) Burning + dilute HCl; iv) Base digestion. Red arrows indicate zones of alteration. Image d) shows a pattern of corrosion produced by base digestion on a shard of Hekla 1341 glass. Image a) iv. is an optical image – all useful shards of Katla 1357 were considerably degraded through base digestion, and were not clearly visible through SEM imagery.

Figure 2: Selected TAS diagrams showing group variations in geochemical classifications following chemical treatments of volcanic glass. Purple circles – control group; red diamonds – burning + dilute HCl; green squares – acid digestion; yellow stars – base digestion. These examples were selected for the clarity of variation from the untreated group across a range of SiO₂ contents. Sample RL1 has been included to variation across initial composition within a single sample. TAS classification after Le Bas et al., 1986.

Figure 3: Boxplots and ternary diagrams displaying variations in major element geochemistry for a) Katla 1357; b) Hekla 1947; c) Lipari glass. Symbols are coloured as follows: purple – control group; red – burning + HCl; green – acid digestion; yellow – base digestion.

Table 2: PERMANOVA results

Table 3: Summary of variations in relative oxide concentration against average SiO₂ content in control group, NBO/T, and H₂O by difference. Statistically significant ($P < 0.01$) variations are highlighted in bold. As comparisons are drawn between normalised results, constant sum effects should be taken into account.

Figure 4. Composite TAS diagram showing the range of reported Icelandic geochemistry against geochemical variations produced by chemical extraction in this study. This study: green squares – acid digestion; orange diamonds – burning + HCl; yellow stars – base digestion. Existing literature is denoted with circle symbols. Grey – Plunkett & Pilcher (2018) (assigned 'Icelandic'). Red – Plunkett & Pilcher (2018) (assigned 'non-Icelandic'). Purple – Pilcher et al. (2005) (selected Borge tephtras). Blue – composite Icelandic data from Mangerud et al. (1984); Mangerud, Furnes & Johansen (1986); Pilcher, Hall & McCormac (1996); Boygle (1994); Dugmore et al. (1992); Dugmore, Larsen & Newton (1995); Dugmore & Newton (1997), Larsen, Dugmore et al. (1999); Wastegard et al. (2001); Hall & Pilcher (2002); Chambers et al. (2004); Swindles (2006); Davies et al. (2007); Rea, Swindles & Roe (2012); Ratcliffe et

1 al. (2017). Cyan – composite Katla data from Boyle (1994); Streeter & Dugmore
2 (2014).
3

4 Table A.1. Major element geochemistries of tephra analyses for each chemical
5 treatment, normalised to 100%. Analyses with an original total oxide count of < 97 %
6 have been removed. (Supplied as a separate file)

7

8 Table A.2. Secondary glass standards for EPMA (non-normalised) (Supplied as a
9 separate file)