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Standard chemical-based tephra extraction methods significantly alter the geochemistry of volcanic glass shards

Claire L. Cooper[*1,2], Ivan P. Savov[2], Graeme T. Swindles[1,3]

[1] School of Geography, University of Leeds, UK, LS2 9JT

[2] School of Earth and Environment, University of Leeds, UK, LS2 9JT

[3] Ottawa-Carleton Geoscience Centre and Department of Earth Sciences, Carleton University, Canada

[*] Corresponding author: gyclc@leeds.ac.uk

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Abstract

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

1 Introduction

The reliable and non-destructive extraction of tephra is essential for modern applications of tephrochronology and volcanology (Lowe, 2011; Watson et al. 2015). While many methods have been proposed and practiced for the separation of tephra from peat and lake sediments (Hall & Pilcher, 2002; Blockley et al. 2005; Newton et al. 2005), doubts have been raised concerning the geochemical alteration of volcanic glass through these processes. In particular, the use of acid digestion methods has been indicated in the formation of alteration zones around small glass shards, resulting in complications when performing scanning electron microscopy (SEM) or electron probe microanalysis (EPMA) (Blockey et al. 2005). These effects are notably more pronounced in the case of smaller glass shards, producing significant difficulties in the field of tephrochronology where the use of cryptotephra (studies utilising glass shards < 150 µm) is becoming increasingly common for the dating and correlation of sediment and volcanic successions (Watson et al. 2016). Attempts have been made to challenge these claims (Roland et al. 2015); however, this initial case study focused purely on rhyolitic tephra (silica-rich distal deposits of Hekla 4), which comprises slightly more than 75% of the cryptotephra compositions found in western Europe (Swindles et al. 2011; Swindles et al. 2017), and acknowledged that further work on a greater range of glass compositions was required. The ability to accurately compile geochemical profiles of tephra shards is crucial in the identification and correlation of tephra layers to produce isochrons within sediment columns; glass alteration introduces an element of uncertainty which may compromise the reliability of analytical results and their interpretations (Roland et al. 2015; Watson et al. 2016). Several attempts have been made to introduce less chemically destructive techniques, most notably the density separation technique of Blockley et al. (2005). However, the effectiveness of these techniques in removing unwanted biogenic and organic material, such as plant detritus, peat, and biogenic silica, is variable in comparison to traditional chemical digestion-based methods (Brewer et al., 2008; Roland et al., 2015). Therefore, while the original chemical composition of individual shards may be better preserved through density separation techniques, imaging and spectral analysis of samples may still be impaired by low shard recovery rates produced by repeated separation procedures (Roland et al., 2015). This trade-off between shard concentration and geochemical purity of the glass is the cause of dispute, all the more so as the differing methods have not been thoroughly and comprehensively tested against each other.

Additionally, the apparent preferential preservation of rhyolitic over basaltic tephra in European lake and peatland sites has previously been highlighted by several studies (Wastegård & Davies, 2009; Lawson et al. 2012; Watson et al. 2017). Despite the high frequency of mafic volcanic activity in Iceland (the primary source of European distal tephra deposits (Lawson et al. 2012)), < 3 % of tephras found in western European sites have a basaltic composition (Swindles et al. 2017). Similar distributions of distal tephra are found in other regions globally – a study of tephra found in several Japanese marine cores found that > 80 % of tephra layers contained > 65 % silica (dacites/rhyolites) (Schindlbeck et al. 2018), and of the 3171 tephras reported from the Kamchatsky Peninsula (Far-East Russia; Ponomareva et al. (2017)), only 30% contained < 65 % silica (basalts,andesites and dacites). Several possible explanations have been proposed for this discrepancy – firstly, that basaltic material is often a product of less explosive volcanism, resulting in less widespread distribution (Dugmore et al. 1995); secondly, that the higher density of basaltic tephra shards causes them to deposit as fallout more rapidly than rhyolitic shards, resulting in lower concentrations of mafic material at greater distances (Stevenson et al. 2015); and thirdly, that basaltic glass is more susceptible to alteration and hydration processes in acidic environments, such as those found in peatland or produced during traditional sample preparation techniques (Pollard et al. 2003; Blockley et al. 2005). As the historical tephra record in Europe is relatively well-documented (Swindles, 2011; Lawson et al. 2012), many recent studies have focused on extending the tephra record into older sequences, including tephras from the early Holocene and Younger Dryas periods (Swindles et al. 2017). If the latter hypothesis is correct, many older tephras, particularly those with a more mafic geochemistry, are likely to be more significantly altered from their initial composition.

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

2 Materials and Methods

2.1 Tephra samples

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

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

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

2.2 Processing methods

2.2.1 Control (No treatment)

Samples in the control group were not subjected to any chemical treatment following the combination of the glass with peat. Samples were washed through a 16 µm sieve with deionised water and then dried at 105 ˚C prior to electron probe analysis. While density separation techniques are becoming a common procedure in the field of tephrochronology, none were performed at any stage in this study as the process is rarely used in combination with acid or base treatments (Blockley et al., 2005).

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

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

2.2.3 Acid digestion (Method 2)

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

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

2.2.4 Acid/base digestion (Method 3)

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

The samples in this study were placed in 500 ml beakers with 150 ml of 1M HCl, and heated to 80˚C for 2 hours. The samples were then cooled to room temperature over the course of 30 minutes and rinsed with deionised water, before being transferred to clean beakers. 150 ml of 0.5M KOH was then added, and the samples were again heated to 80 ˚C for 2 hours. Following this, 10-30 ml of deionised water was added in small increments until no further material was extracted, and the mixtures were then cooled to room temperature as before, and rinsed through a 10 µm mesh with 500 ml of deionised water before being returned to their beakers. A further 150 ml of 1M HCl was then added to the samples, which were then heated again to 80˚C for 5 hours. The samples were then cooled and rinsed, washed through a 16 µm sieve, centrifuged at 3000 rpm for 10 minutes, and the supernatant pipetted off.

2.3 Electron Probe Microanalysis

The samples were dried and mounted on 25.5 mm disks in Epo-Tek® resin, and finished with a 0.25 µm diamond polish to ensure exposure and a polished surface. EPMA was performed at the Tephra Analysis Unit at the University of Edinburgh, using the "combined analysis method" described in detail in Hayward (2012). All analyses were performed using a 5 µm diameter beam of 15 kV, varying only the current between 2 nA for Na, Mg, Al, Si, K, Ca, and Fe quantities, and 80 nA for Ti and Mn. Secondary (external) glass standards (basalt BCR-2G and Lipari rhyolite) were analysed before each EPMA run, and a PAP correction applied. Analyses were performed as close to the centre of each shard (i.e. the centre point of the x and y axes) as possible in order to ensure accurate geochemical profiling of the glass, in accordance with standard laboratory procedures. Shards that were not sufficiently exposed across the polished surface were excluded.

2.4 Statistical Analysis – PERMANOVA

PERMANOVA is a non-parametric multivariate method of statistical analysis. Originally developed as an adaptation of traditional MANOVA methods (Anderson, 2001; McArdle & Anderson, 2005) to better suit the non-normal distributions and discrete (rather than continuous) data values found in ecological datasets (while ecological datasets were the intended target, the developers stated that the method was likely to be applicable across the natural sciences; Anderson, 2001), PERMANOVA is most applicable when handling datasets with asymmetric distributions, and in variables containing multiple zeros. It is therefore useful in the comparison of diverse geochemical profiles, in which element distributions are unlikely to follow a pattern of normal distribution.

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

3 Results

3.1 Notes on removal of organic material

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

3.2 Glass Alteration

3.2.1 Glass Morphology

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

[Insert 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.]

The evidence gathered in this study strongly indicates that underlying glass geochemistry plays a role in the degree of shard alteration. Shards from the basaltic Katla 1357 (K1357) eruption (average SiO_2 ~ 48 wt %; figure 1 (a)) show notably greater morphological changes as a result of each treatment than those shards with a higher silica content, such as the andesitic Hekla 1991 (average SiO_2 content 56.48 %; figure 1 (b)), or the rhyolitic Lipari obsidian (SiO_2 ~75 wt %; figure 1 (c)). The dissolution of the K1357 shards following base digestion (method 3) was sufficiently extensive to entirely prohibit the use of EPMA in that sample, while the Lipari obsidian was unusual in that it exhibited no alteration rim following weak or concentrated acid treatment, and only a narrow rim of 5-8 µm following base digestion.

3.2.2 Geochemistry

[insert 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 SiO_2 contents. Sample RL1 has been included to variation across initial composition within a single sample. TAS classification after Le Bas et al., 1986.]

Our results show a large amount of variability in glass geochemistry following chemical treatment. While many oxide concentrations show significant variation across treatments (discussed further in section 3.3), the most consistently significant differences, both positive and negative, occur in the concentrations of Na_2O, CaO, K_2O, MgO, and SiO_2. While mean relative concentrations of Na_2O and K_2O typically decrease following chemical treatment of the glasses, the relative concentrations of

SiO_2, MgO, and CaO typically increase. Additionally, there is a clear and persistent trend across almost all major element oxides wherein variation compared to the control group is greater following acid and base digestions (methods 2 and 3) than those subjected to method 1. The four exceptions to this trend are: the Lipari glass, which displays very few variations in mean oxide concentration to a statistically significant level (5%) of any major element under any tested conditions (the exception being method 2, which produced a 5.52% increase in mean FeO content); and the SL1, RL1, and Hekla 1991 samples, in which the initial geochemistry was found to be variable. In these cases, significant statistical deviations from the control group may simply be a result of variability within the natural glass shard population. A full summary of major element geochemistry and secondary samples can be found in appendix 1.

[Insert 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.]

In addition to the trend described above, we also find a correlation in responses to chemical treatment with initial SiO_2 abundances (i.e. the composition of the control group). The examples shown in figure 3 summarise the geochemical alterations to a basalt, andesite, and rhyolite respectively. In the basaltic K1357 sample (average initial SiO_2 = 47.6 wt %), the mean Na_2O content varies negatively by 61.7 % following acid digestion (method 2) when compared to the control group. In the andesitic Hekla 1947 (average initial SiO_2 = 61.5 wt %), the Na_2O concentration decreases between the control and acid digestion treatment by 5.7 %, and in the rhyolitic Lipari glass (SiO_2 = 75.1 wt %) the decrease in the mean concentration is as low as 0.667 %. Following base digestion (method 3), the Na_2O content deviates negatively from the control group by 26 % for Katla 1357, 38.2 % for Hekla 1947, and 0.48 % for Lipari glass. Both the basalt and the andesite display significantly more variation across groups when compared with the rhyolite.

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

3.2.3 PERMANOVA

Table 2 shows the results of the PERMANOVA analysis of each method in comparison to the oxide quantities measured in the control group. In this instance we regard a *P* value of < 0.01 (1 %) to be statistically significant, i.e. indicating that the wt% of that element has changed to a significant degree. Our results confirm that the most consistently variable oxide is K_2O, which shows a significant within-group variation in 8 out of 30 analyses. CaO and SiO_2 both show significant within-group variation in 7 of 30 analyses, and Na_2O, MgO, MnO, and TiO_2 each show significant variation in 5 of 30. Additionally, samples which show significant variation in at least one oxide across all three chemical treatments show fewer variations, and less significant variance (lower *F* values), in the method 1 treatment group than in either the acid or base digestion groups (methods 2 and 3).

The PERMANOVA analysis also allows comparison between sample groups. For example, while the Hekla-Selsund Phase 2 sample (average SiO_2 content 53.6 %) shows four statistically significant variations in major element oxide concentrations (K_2O, CaO, SiO_2, and TiO_2) following methods 2 and 3, and two following method 1 (TiO_2 and MnO), the Lipari glass samples do not show statistically significant variations in any oxide following any treatment. Comparison of samples with contrasting SiO_2 content (see table 3), reveals a broad pattern of lower susceptibility to chemical alteration with increasing silica content.

[Insert Table 2: PERMANOVA results]

[Insert Table 3: Summary of variations in relative oxide concentration against average SiO_2 content in control group, NBO/T, and H_2O 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.]

4 Discussion

This study confirms persistent assertions within tephrochronology that substantial chemical alteration of volcanic glass via commonly used extraction techniques, namely the acid digestion method, is possible, particularly for basaltic and low-silica andesitic tephras (< ~60% SiO_2; Blockley et al, 2005). The assertion of Roland et al. (2015) that no significant geochemical variation could be found following acid digestion is supported by our findings, as the felsic samples (> 63% SiO_2) in our study were among the least susceptible to geochemical alteration. In particular, the highly silicic Lipari glasses were by far the least prone to any chemical perturbation. While the precise mechanisms behind this relationship require further study, we suggest that the increased polymerisation of silica chains in rhyolitic glass may provide a stabilising factor, preventing the leaching of mobile elements (Iler, 1979; Chan, 1989; Dultz et al, 2016). Furthermore, while outside the scope of the data presented in this study, it is likely that volatile content of the tephra could affect the susceptibility of the glasses to alteration, as the formation of molecules such as OH^- and CO_3^{2-} (for example) reduce the degree of glass polymerisation.

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

Also of note is the apparently consistent creation in some samples of novel glass geochemistry – in other words, instances in which the combined variation in one or more major element weight percentages is significant enough to place multiple glass shards in new geochemical category when plotting against standard TAS definitions. This is especially relevant for studies concerning cryptotephra < 30-50 µm in diameter (frequently encountered in distal tephra studies; Lowe et al., 2011; Pearce et al., 2014), or those with a high surface area-to-volume ratio, such as tricuspate shards or those with multiple bubble walls, as any alteration in those instances is likely to affect a greater percentage of the glass composition in those shards. Particularly important are those compositions which transition from sub-alkaline to alkaline fields. These alkaline compositions are only rarely erupted in Iceland (Wood, 1978; Nicholson et al. 1991; Gudmundsdóttir et al. 2018), yet are occasionally reported in European cryptotephra studies which variably attribute the material to Icelandic eruptions or suggest ultradistal sources, such as the Cascade Range or Alaskan volcanoes of North America (Jensen et al., 2014; van der Bilt et al., 2017; Plunkett & Pilcher, 2018). Figure 4 shows a composite TAS diagram combining several reported Icelandic cryptotephras, overlain with selected anomalous results from this study. While some analyses are clearly distinguishable from the wider trend of Icelandic geochemistry, many of the variations produced by all three treatment methods fall well within the boundaries of reported Icelandic trachyandesites in the European tephra record. Although it is possible that these reported analyses represent the original geochemistry of the tephra shard in question, the control groups for each of the anomalous trachyandesites and trachytes found in this study did not fall into either geochemical category. It is therefore also possible that some reported trachyandesites may have been unintentionally manufactured as a result of chemical alteration during extraction. Great care should therefore be taken in the interpretation of apparently ultra-distal tephras, particularly regarding the relative contents of groups I and II oxides (K_2O, Na_2O, CaO, MgO), which we find to be particularly susceptible to alteration. It is however possible that this same susceptibility may have applications in assessing the validity of volcanic glass datasets, although the exact nature of any potential statistical test based on that data is beyond the scope of this study.

[Insert 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 tephras). 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 al. (2017). Cyan – composite Katla data from Boygle (1994); Streeter & Dugmore (2014).]

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

5 Conclusions

[1] The use of burning & dilute HCl, concentrated H_2SO_4 and HNO_3 (as used in the common acid digestion method of tephra preparation), and concentrated KOH in the extraction of volcanic glass are all sufficient to cause statistically significant variations in the less stable element oxides;

[2] The oxides most susceptible to variation are K_2O, CaO, SiO_2, and Na_2O. The most statistically stable oxides are Al_2O_3 and FeO.

[3] Basaltic and basaltic andesitic glasses are most susceptible to alteration through exposure to concentrated acidic (HNO_3, H_2SO_4) and basic (KOH) conditions;

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

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

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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 SiO_2 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 SiO_2 content in control group, NBO/T, and H_2O 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 tephras). 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

al. (2017). Cyan – composite Katla data from Boygle (1994); Streeter & Dugmore (2014).

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

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