

$^{40}\text{Ar}/^{39}\text{Ar}$ ages and residual volatile contents in degassed subaerial and
subglacial glassy volcanic rocks from Iceland

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ABSTRACT

Major volatile contents (H_2O , CO_2 , F, Cl, and S) and $^{40}\text{Ar}/^{39}\text{Ar}$ ages have been determined in variably degassed rhyolite obsidians from Pleistocene-Holocene aged subaerial and subglacial eruption environments from the Torfajökull volcanic center and the monogenetic volcano at Prestahnúkur (Iceland). Icelandic subglacial rhyolites preserved residual H_2O contents of 0.08 - 0.69 wt. %, non-detectable CO_2 , 840 - 1780 ppm F, 430 - 2000 ppm Cl and 6 - 45 ppm S. Most subglacial obsidians show degassed volatile signatures at the time of their eruption under ice. One eruption (Bláhnúkur, Torfajökull), showed H_2O contents which exceed those expected for quenching at atmospheric pressures (up to 0.69 wt. % H_2O) and are consistent with eruption at ~ 40 kbar pressure or equivalent to under ~ 450 m of ice. Altered and microcrystalline groundmass in some subglacial rhyolites yield variable volatile contents likely the result of micro-scale variability and the presence of alteration products. Two subaerial rhyolite obsidians gave low, volatile contents consistent with quenching at the surface. New $^{40}\text{Ar}/^{39}\text{Ar}$ ages were determined on the subglacially erupted rhyolites and provide constraints on the timing and frequency of glacio-volcanism during the Pleistocene. Three subglacial eruptions at Torfajökull yielded ages of 108 ± 22 ka (Bláhnúkur), 255 ± 20 ka (Hábarmur) and 236 ± 7 ka (Háskerðingur) which fit into a range of previously determined ages at Torfajökull of 67 -384 ka. A new age of 132 ± 19 ka was determined for the monogenetic subglacial eruption at Prestahnúkur. Holocene aged subaerial volcanic glass produced no ages due large amounts of air-derived ^{40}Ar (84-93%). Preliminary apparent $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the limited feldspar phenocrysts available in these crystal-poor samples yield erroneous apparent plateau ages far older than eruption ages suggesting a homogenously distributed excess Ar component which can potentially be correlated with ice thickness. Our observations indicate that unaltered, subglacially erupted glasses that are partially to wholly degassed are promising materials for the application of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer. The precision to which we can date these young glassy samples currently limits the use of Ar/Ar as a tool for understanding the exact timing and duration of glaciovolcanism in the recent past.

Keywords $^{40}\text{Ar}/^{39}\text{Ar}$ dating, volatiles, NanoSIMS, subglacial eruption, volcanic glass, geochronology.

1. INTRODUCTION

Quaternary glaciations have greatly affected the morphology and evolution of volcanic systems in Iceland (Björnsson and Pálsson, 2008; Eriksson, 2008; Norddhal et al., 2008). During ice-free periods, subaerial volcanism produced lava fields and accompanying tephra deposits, while during glacial periods, prominent tuyas (table mountains) and ridges, along with constructive edifices at central volcanoes, were produced during subglacial eruptions. Subglacial eruptions are often more variable than subaerial eruptions due to the complex interactions between the erupting material and ice, water and steam (e.g. Tuffen et al., 2001). The nature of the volcano-ice interaction can also evolve over the duration of an eruption in a rapid manner both spatially and temporally depending on temperature changes, magma discharge rate, pressure, ice thickness, presence of melt-water, as well as magma rheology (McGarvie, 2009). Important information about the timing and duration of glacial and interglacial periods in the recent past can possibly be derived from dating volcanic deposits that have interacted with ice (see review by McGarvie, 2009).

The $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique is an important tool for determining ages of Quaternary volcanic rocks. Application of this technique to deposits that lack the necessary K-rich phenocrysts is often challenging. In such cases, it is necessary to use other eruption products, such as volcanic glass, to constrain the timing of volcanism. However, $^{40}\text{Ar}/^{39}\text{Ar}$ dating of glassy materials is traditionally avoided due to the associated analytical complications. These include the hydration and alteration of glass, leaching of alkalis, and Ar-loss from a ‘leaky’ glass structure (Noble, 1967; Kaneoka, 1972; Foland et al., 1993). Recent successes in applying the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer to volcanic glass (e.g., Flude, 2005; McGarvie et al., 2006, 2007; Brown et al., 2009; Morgan et al., 2009; Flude et al., 2008, 2010) have advanced our understanding of the behavior of Ar upon eruption and quenching of melt. Yet despite these advances, the analytical

limitations imposed by the inherently young age of Quaternary deposits (i.e., very small amounts of radiogenic ^{40}Ar in-growth and often small amounts of ^{36}Ar) remain. Our current understanding of what factors may be important in determining the suitability of glassy materials for $^{40}\text{Ar}/^{39}\text{Ar}$ dating (e.g., magma chemistry, volatile contents, eruption mechanism, degassing behavior, etc.) is limited.

In this study, we investigate $^{40}\text{Ar}/^{39}\text{Ar}$ and major volatile contents (H_2O , CO_2 , Cl , F , and S) in a suite of effusion-dominated rhyolites from several subglacial (Torfajökull and Prestahnúkur, Iceland) and one subaerial eruption (Hrafninnusker, Torfajökull) that are chemically and texturally distinct to better understand the application of the $^{40}\text{Ar}/^{39}\text{Ar}$ system to glassy materials. Volatile contents preserved in fresh volcanic glass can provide a *minimum* estimate of the pre-eruptive volatile contents of the original magma from which they are derived, as well as track and record the degassing history of a body of magma through time (Johnson et al., 1994; Balconne-Boissard et al., 2010). Here, we look at the preserved volatile record to assess variability and the occurrence of poor or incorrect $^{40}\text{Ar}/^{39}\text{Ar}$ ages to evaluate the suitability of young, subglacial and subaerially erupted glassy material for $^{40}\text{Ar}/^{39}\text{Ar}$ dating.

2. SAMPLE LOCATIONS AND ERUPTION ENVIRONMENT

Eruption products from two volcanic centers in Iceland were sampled: (1) predominantly subglacial rhyolites from Torfajökull (**Fig. 1a, b**) and (2) a small-volume (0.6 km^3 ; McGarvie et al., 2007) subglacial rhyolite eruption of a single magma-batch at Prestahnúkur (**Fig. 1a, c**). Eruptions at both locations have involved complex volcano-ice interactions (e.g., Tuffen et al., 2001; McGarvie et al., 2006, 2007).

2.1 Torfajökull

The Torfajökull central volcano is located in Iceland's Southern Flank Zone – a volcanic zone in which active spreading is either absent or minor, and which is dominated by well-developed volcanic centers

characterized by a higher proportion of silicic (and intermediate) rocks of transitional to alkaline composition (see reviews by Jakobsson et al., 2008; and McGarvie, 2009). Torfajökull is an elongate (30 km by 18 km) and dissected rhyolite plateau ca. 450 km² in area with a volume of ca. 250 km³ and is the largest active rhyolitic volcanic center in Iceland (**Fig.1a** and **Fig. 1b**; Sæmundsson, 1977; McGarvie, 1984; Macdonald et al., 1990). Approximately ten rhyolite eruptions have occurred throughout the Holocene; the most recent being in 1477 AD (Larsen, 1984). However, subglacial rhyolite formations dominate and testify to the sustained presence of ice during the Quaternary glacial periods (McGarvie, 2009). It is not known when Torfajökull first became active, and although the longevity of Icelandic volcanic systems is estimated to be 0.5-1.0 Ma (Sæmundsson, 1978; Flude et al. 2008) these estimates are poorly constrained and rely on palaeomagnetic information. Petrogenetic models to explain the formation of the high volume of rhyolitic magmas as found at Torfajökull from an oceanic environment include: fractional crystallization of basaltic magma (Furman et al., 1992); fractional crystallization accompanied by magma mixing processes (Sigurdsson and Sparks, 1981; McGarvie, 1984; Macdonald et al., 1987; Jónasson, 1994); and partial melting of evolved extrusive and intrusive rocks (Gunnarsson et al., 1998; Sigmarsson et al., 2008). There is no agreed consensus on the origins of Torfajökull's rhyolitic magmas, and evidence suggests that possibly all of the above processes have operated to varying degrees at different times during the evolution of this magma system (see Jónasson, 2007).

The majority of Torfajökull rhyolites investigated in the current study (**Table 1**) are the products of subglacial eruptions, with the exception of two Holocene obsidians from Hrafninnusker (samples HSK-12 and HSK-32, see below), a compositionally-zoned eruption which took place in the early Holocene (McGarvie et al., 1990). The subglacial rhyolite samples include the well-studied edifice of Bláhnúkur (e.g., Tuffen et al., 2001; 2002), as well as rhyolites samples from the subglacial mountains of Háskerðingur, Kaldaklofsjöll and Hábarmur (McGarvie et al., 2006). Samples are described briefly below and in the **Supplementary Materials** (see also summary in **Table 1**).

Háskerðingur, Kaldaklofsfjöll, and Hábarmur (Pleistocene, subglacial): The subglacial sample from Háskerðingur (TJ/98-6) is a rhyolite obsidian vitrophyre from a subglacial dome with low crystal contents (<10%). Sample TJ/98-50 (Kaldaklofsfjöll) is a glass-bearing pheno-pantellerite. It contains both aegirine and aenigmatite $[(\text{Na,Ca})_4(\text{Fe}^{2+}\text{Ti,Mg})_{12}\text{Si}_{12}\text{O}_{40}]$, and the groundmass appears mildly altered in thin section. Samples TJ/97-14 and TJ/97-15 (both from Hábarmur) are chemically similar samples, though TJ/97-15 is an aphyric obsidian while TJ/97-14 is hydrothermally altered (partially zeolitized) glass-bearing rhyolite with a sugary microcrystalline groundmass texture. With this suite of samples we investigate the effects of variable magma chemistry and hydrothermal alteration on age determination.

Bláhnúkur: Subglacial samples from Bláhnúkur (TJ/98-39 and TJ/98-40) come from a small volume (~0.1 km³) ~350 m high rhyolitic edifice that forms a drape over the summit region of a pre-existing mountain (Tuffen et al., 2001; McGarvie, 2009). Bláhnúkur has been interpreted as the product of an entirely effusive eruption (i.e., magmatically-fragmented lithofacies are absent). Sample TJ/98-40 is rhyolite obsidian vitrophyre while TJ/98-39 is a glass-bearing microcrystalline rhyolite from the same lava lobe. Given that Bláhnúkur rises 350 m above surrounding terrain and lacks a subaerial lava cap, Tuffen et al. (2002) concluded that the minimum thickness of ice present at the time of eruption was therefore at least 400 m. The samples from Bláhnúkur allow us to investigate chemically identical, texturally diverse subglacial eruption products.

Hrafninnusker (Holocene, subaerial): Samples HSK-12 and HSK-32 are aphyric rhyolitic obsidians from the Hrafninnusker eruption (McGarvie, 1984; McGarvie et al., 1990). This eruption produced substantial lava flows suggesting that it either took place during the completely ice-free conditions of the Holocene or during the transition period as ice was rapidly melting and retreating at the end of the last (Weichselian) glacial period. Hrafninnusker is the largest of Torfajökull's Holocene rhyolite eruptions (~0.3 km³; McGarvie, 1984) and after an initial explosive phase that produced a proximal tephra pile ~40 m thick, four vents effused seven lava lobes that reached up to 2.5 km from the vents (McGarvie et al.,

1990). A notable feature of Hrafninnusker is that it is compositionally zoned to an extent which is unusual for Icelandic rhyolite eruptions (McGarvie et al., 1990). Sample HSK-12 occurred early in the eruption sequence and is more evolved than the later erupted HSK-32. There is no evidence to suggest that the samples have undergone any post-emplacement modifications, such as hydration and alteration, which is common elsewhere in rhyolitic rocks (Macdonald et al., 1990). They represent the only subaerially erupted rhyolites from Iceland investigated in this study. Hrafninnusker allows us to test the $^{40}\text{Ar}/^{39}\text{Ar}$ method on fresh, young obsidians from a subaerial environment.

There are limited geochronological studies focused on Torfajökull eruptives, largely due to the lack of abundant and suitable K-rich phenocrysts in the eruption products. A previous $^{40}\text{Ar}/^{39}\text{Ar}$ pilot study by McGarvie et al. (2006), however, determined eruption ages at Torfajökull ranging from 67 ± 9 to 384 ± 20 ka (though these ages do not represent absolute age end-members, i.e., Holocene eruptions are present), with the latter representing an age for Hábarmur (samples TJ/97-14, TJ/97-15 in this study) (**Table 1**). See **section 5.2** for discussion.

2.2 Prestahnúkur, Iceland

Prestahnúkur is interpreted as a wholly effusive rhyolite eruption into an ice sheet of estimated 700 m minimum thickness (McGarvie et al., 2007). Assumed discharge rates of 1 to $10 \text{ m}^3\text{s}^{-1}$ give an eruption duration spanning 2 to 19 years (McGarvie et al., 2007). The lack of products indicating magmatic fragmentation and an absence of subaerial features suggest that the eruption occurred entirely under ice (McGarvie, 2009). With Prestahnúkur, we investigate an evolved, small eruptive unit from a subglacial environment. Three rhyolitic obsidian vitrophyres from Prestahnúkur were analyzed: PK-1, PK-6 and PK-7 (**Fig. 1c**). The Prestahnúkur rhyolites have low, average average crystal contents of $< 8\%$ (McGarvie et al., 2007), and a generalized mineral assemblage of feldspar + clinopyroxene + olivine + ilmenite +/- allanite. Feldspar is the dominant phase, comprising $\sim 80\%$ of the phenocrysts. The feldspars are

oligoclase in composition (Ab_{70-71}) and occur predominantly as lath and tabular-shaped phenocrysts. Phenocrysts range up to 2 mm in size, but most are around 1 mm in size and rarely larger grains up to 4 mm in size are observed. Olivines (fayalitic) range from Fa_{98} to Fa_{99} . The near-uniform compositions of all samples led McGarvie et al. (2007) to interpret the eruption as formed from a single magma batch. McGarvie et al. (2007) produced $^{40}\text{Ar}/^{39}\text{Ar}$ ages from furnace heating of glass splits from samples PK-1 and PK-7 which gave an isochron age of 89 ± 24 ka (1σ) (**Table 1**).

3. SAMPLE PREPARATION AND ANALYTICAL DETAILS

3.1 Whole rock (XRF) Chemistry

Whole rock chemistry was determined by XRF analyses at the Open University (**Table 2** and **Fig. 2**) using an ARL 8420+ dual goniometer wavelength dispersive XRF spectrometer with 3 kW Rh anode end-window X-ray tube for major and trace elements analyses. The instrument is equipped with five diffraction crystals: LiF220, LiF200, AX06, PET, and Ge111. Typical precisions of major element determinations are 0.2-0.7 % (Ramsey et al., 1995) and standard reference materials WS-E (dolerite) and OU-3 (microgranite) were used.

3.2 Secondary Ionization Mass Spectrometry (SIMS)

All volatile measurements were made using the Cameca NanoSIMS 50 L at the Open University. Sample preparation and analytical parameters are detailed in Clay et al. (2013) and follow those methods given in Hauri et al. (2002) and Saal et al. (2008). Standards for volatile measurements used in this study consisted of NIST standard reference materials (SRM) 610 and 612 and basaltic glass geo-reference materials, ALV-519-4-1, GL-D30-1 and GL-D52-5. A synthetic forsterite and San Carlos olivine were used to estimate the detection limits for each session, which were conservatively determined to be: $\text{H}_2\text{O} \sim 60$

ppm; CO₂ ~ 12 ppm; F ~ 5 ppm; Cl ~ 5 ppm and S ~ 5 ppm. Calibration line data from analysis of glass standards to calculate all volatile contents are given in Clay et al. (2013).

3.3 ⁴⁰Ar/³⁹Ar measurements

Several splits of about 50-100 mg of each sample were picked under a binocular microscope from a 180-250 µm size fraction. This size fraction is small enough to allow optical selection of unaltered glass chips to minimize any effects of analyzing altered material, but large enough to avoid any potential recoil effects during irradiation. Glass shards were ultrasonically cleaned in cold, weak acid (2 % HNO₃) or solvent (acetone), followed by de-ionized water prior to irradiation. ⁴⁰Ar/³⁹Ar step-heating experiments were undertaken using a MAP-215-50 noble gas mass spectrometer at the Open University. Samples and standards were cleaned and loaded into aluminum foil pouches and irradiated at McMaster Reactor, Canada, for ~ 1 hour. GA-1550 (biotite, age = 98.5 ± 0.5 Ma; McDougall and Wellman, 2011) and TCR-2 (Taylor Creek Rhyolite; sanidine, age = 28.26 ± 0.02 Ma, Kuiper et al., 2004) were used as neutron fluence monitors and placed between every 10 samples. Approximately 25-50 grains were loaded into aluminum sample holders. Released gases were passed through a liquid nitrogen cooled ball bearing-filled u-tube, trapping most active gases, particularly longer chain hydrocarbons. Released gases were then exposed to two SAES getters (one running at 400 °C and the other at room temperature) for 5 minutes. A New Wave Nd-YAG 1064 nm infrared laser was used for all step heating experiments, and glass separates were evenly and slowly heated incrementally until fused to completion (typically in 7-12 steps). Fifteen measurements were made per cycle for each isotope with a total of ten cycles. ⁴⁰Ar/³⁹Ar errors quoted are 2σ. Data were corrected for instrument blanks, mass discrimination, decay of ³⁷Ar and ³⁹Ar and reactor-induced interferences on ⁴⁰Ar, ³⁹Ar and ³⁶Ar (all correction factors provided in the **Supplementary Materials**).

4. RESULTS

4.1 Whole rock chemistry

The composition of Torfajökull rhyolites and three Prestahnúkur rhyolites are given on a total-alkali-silica (TAS) plot (**Fig. 2a**; Le Bas et al., 1986) grouped by eruption unit. Whole rock chemistry is given in **Table 2**. All samples lie in the rhyolite field of the TAS plot (**Fig. 2a**; Le Bas et al., 1986) and can be classified further based on the rhyolite classification of Macdonald et al. 1974 (**Fig. 2b**). Agpaitic index (molar $\text{Na}_2\text{O}+\text{K}_2\text{O}/\text{Al}_2\text{O}_3$) calculations (**Supplementary Materials**) show that all Torfajökull rhyolites are broadly subalkaline-peralkaline and that TJ/98-50 is the most evolved and only pantelleritic rhyolite (TJ/97-14 borders pantellerite and commenditic rhyolite). All subglacial samples were previously analyzed for whole rock chemistry (McGarvie et al., 2006; 2007) and comparisons with this study agree within ~2 %. Prestahnúkur rhyolites are amongst the most silica-rich rhyolites in Iceland, with SiO_2 contents up to 76.4 wt. % (PK-6). Results for PK-1 and PK-6 are in agreement with those of McGarvie et al. (2007) within << 1%. The analysis of PK-7 from this study, however, seems anomalous, varying by up to several weight % in Fe_2O_3 , Al_2O_3 , Na_2O and K_2O from PK-1 and PK-6 as well as the PK-7 analysis from McGarvie et al (2007). We reject this discrepant analysis and use instead the value from McGarvie et al. (2007).

4.2 Volatiles

Average volatile contents (H_2O , CO_2 , F, Cl and S) for each sample are presented in **Table 3** and **Figure 3**. Short interpretations are included here, as data for individual samples are not discussed in detail elsewhere. Further discussion of the sample set as a whole is presented in **Section 5.1**.

4.2.1 Torfajökull

Samples from Bláhnúkur (TJ/98-39 and 40) yielded differing volatile element results. TJ/98-40 contained 0.69 ± 0.01 wt. % H_2O , non-detectable CO_2 , 1690 ± 40 ppm F, 2000 ± 120 ppm Cl and 6 ± 1 ppm S. this sample yielded homogenous results over six repeat analyses, with a narrow range in all volatile concentrations (**Table 3**). Conversely, TJ/98-39 was heterogeneous (<0.1 wt.% H_2O , <5 ppm CO_2 , 80 ± 5 ppm F, non-detectable Cl and S) with often non-detectable volatiles, possibly reflecting the microcrystalline nature of the sample preserving small-scale volatile heterogeneities over the analytical sample volume (typically $12 \mu\text{m}$). TJ/98-40 is interpreted as a partially degassed rhyolite obsidian (compared to a degassed rhyolite obsidian dome erupted at the surface, typically ~ 0.1 wt. % H_2O and Cl; Dunbar and Kyle, 1992 see **Figure 3a**) giving an elevated H_2O content with eruption and quenching of the Bláhnúkur rhyolite under ice (see discussion **section 5.1**).

Háskerðingur (TJ/98-6) yielded volatile contents of: 0.08 ± 0.01 wt.% H_2O , non-detectable CO_2 , 1650 ± 90 ppm F, 1300 ± 80 ppm Cl and 18 ± 1 ppm S. We consider these to be consistent with degassed obsidian (defined above), quenched upon eruption in a subglacial rhyolite dome. Kaldaklofsjöll (TJ/98-50) groundmass material gave highly variable results revealing chemical heterogeneities. Elevated and highly variable H_2O and CO_2 measurements (**Table 3**) are attributed to micro scale variability associated with heterogeneities present on a scale smaller than that of the analytical sample area ($\leq 12 \mu\text{m}$). This sample cannot reliably provide any information due to this variability. Hábarmur gave variable results between sample TJ/97-14 (altered glass-bearing rhyolite) and TJ/97-15 (aphyric rhyolite obsidian). Volatile contents for sample TJ/97-15 were: 0.09 ± 0.01 wt.% H_2O , non-detectable CO_2 , 1780 ± 40 ppm F, 1620 ± 50 ppm Cl and 45 ± 1 ppm S. TJ/97-15 most likely represents the residual volatile content of a degassed obsidian, consistent with quenching upon subglacial eruption of Hábarmur rhyolite. Sample TJ/97-14 is chemically identical to TJ/97-15 but visibly altered in thin section. Measured volatiles seem consistent with the evidence of alteration by hydrothermal fluids (e.g., non-reproducible, variable on a tens of micron scale) and show significant contamination in the form of elevated CO_2 , likely sequestered in alteration products (e.g., up to 7800 ± 2200 ppm CO_2 ; **Table 3**).

Holocene subaerially erupted Hrafninnusker rhyolitic lavas (samples HSK-12 and HSK-32, Table 3) were relatively homogeneous with regards to all measured volatiles. Measured volatile contents were: 0.08 ± 0.01 and 0.09 ± 0.01 wt.% H_2O , non-detectable CO_2 , 1600 ± 30 and 1740 ± 10 ppm F, 1590 ± 20 and 1760 ± 80 ppm Cl and 10 ± 3 and 45 ± 5 ppm S, respectively. Lack of hydration and alteration, and H_2O contents consistent with quenching at atmospheric pressure suggest these represent degassed subaerial obsidians.

4.2.2 Prestahnúkur

All Prestahnúkur rhyolites yielded consistent values for all measured volatiles with minimal variation from sample to sample. Volatile contents ranged from: 0.11 ± 0.01 to 0.13 ± 0.01 wt.% H_2O , non-detectable CO_2 , 840 ± 10 to 900 ± 10 ppm F, 430 ± 10 to 460 ± 10 ppm Cl and non-detectable S. Such consistency in volatiles may support McGarvie et al.'s (2006) interpretation of Prestahnúkur as a small volume, one-magma batch eruption, or rather a similar degassing history for all samples. These samples appear to represent degassed rhyolite, consistent with quenching at atmospheric pressure (Liu et al., 2005).

4.3 $^{40}\text{Ar}/^{39}\text{Ar}$ Data

The results of step-heating experiments [cumulative release of ^{39}Ar vs. Age (ka)] are presented in **Figure 4**, organized by eruption unit with repeat analyses in individual panels. Selected inverse isochron diagrams ($^{39}\text{Ar}/^{40}\text{Ar}$ vs $^{36}\text{Ar}/^{40}\text{Ar}$) are shown in **Figure 5**. Data for the new ages for Torfajökull and Prestahnúkur are presented in **Table 4**, while the full data set for all experiments is available in the **Supplementary Information** following guidelines recommended in Renne et al. (2009). The criteria used for determining a plateau age follow those recommended in McDougall and Harrison (1999) and

require a minimum of 55% released ^{39}Ar over 3 contiguous steps. Where a ‘recommended age’ for a sample is given (**Table 4** and **Figure 6**), it is a suggestion for the best age of an eruption unit as determined in this study and is calculated as the average of the plateau ages (where plateau ages are in agreement within uncertainty of the determined isochron age).

4.2.1 Torfajökull

Háskerðingur (sample TJ/98-6) was measured in separate glass splits. A plateau age of 232.4 ± 5.7 ka (including 50.9 % ^{39}Ar in the plateau age determination) was determined (**Fig. 4a**) and yielded an isochron age of 216 ± 13 ka with a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ (sub-atmospheric) value of 240 ± 28 . A second plateau age of 239.8 ± 7.0 ka (78.7% of ^{39}Ar) (**Fig. 4b**) was determined and yielded an isochron age of 190 ± 82 ka (**Fig. 5d**) with a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ value of 475 ± 220 . A recommended age (see criteria above) of 236 ± 7 ka is given for Háskerðingur. One feldspar separate was analyzed from Háskerðingur, which yielded an apparent age of 828 ± 8 ka on an inverse isochron (but no plateau age was determined; see discussion in **section 5.2.2**). Step heating experiments were performed on three fractions of whole rock material from Kaldaklofsjöll (TJ/98-50), but large variations existed amongst erroneously old ages across steps (~ 1 -13 Ma) and therefore no age information was determined.

Several separate splits of Hábarmur groundmass and glass (samples TJ/97-14 and TJ/97-15, respectively) were analyzed. One split of glassy sample TJ/97-15 gave a plateau age of 260 ± 24 ka (66.1 % of ^{39}Ar) (**Fig. 4c**) and a second plateau of 249 ± 13 ka (**Fig. 4d**) including 63.7 % ^{39}Ar . A recommended age of 255 ± 20 ka is given for Hábarmur which is ~ 130 ka younger than determined by McGarvie et al. (2006; see discussion). Sample TJ/97-14, did not yield any age information, largely due to variable alteration of the groundmass. Erroneously old ages of ~ 8 -80 Ma were determined for the heavily altered portion of the sample.

Sample TJ/98-40 was measured as separate glass splits which gave plateau ages of 98 ± 20 ka (100 % of ^{39}Ar) and 119 ± 22 ka (80.2 % of ^{39}Ar) (**Fig. 4e and f**). No isochron ages were determined, likely due to large scatter in both the trapped Ar and radiogenic Ar components. Sample TJ/98-39 was analyzed as three whole-rock splits, none of which yielded a plateau or isochron age despite minimal variation in individual age steps. A recommended age of 108 ± 22 ka is given for Bláhnúkur based on TJ/98-40. Sample TJ/98-39 yielded separable feldspar and this sample gave an apparent age of 189 ± 24 ka.

Step-heating analyses of glass shards from samples HSK-12 and HSK-32 did not yield any plateau or isochron ages. Sample HSK-32 showed more variability in step ages than HSK-12. Both samples had large uncertainties on steps often much greater than the ‘apparent age’ particularly for the youngest steps. Between 84-85 % for HSK-32 and 91-93 % for HSK-12 of the total released ^{40}Ar was derived from atmospheric contamination. Use of an inverse isochron did not provide quantitative information as there was too little spread in the data to give information about the composition of trapped Ar.

4.2.2 Prestahnúkur

Sample PK-1 gave plateau ages of 123 ± 16 ka (100 % of ^{39}Ar) and 136 ± 10 ka (100 % of ^{39}Ar) with the latter giving an isochron age of 160 ± 16 ka. A third plateau age of 135 ± 14 ka including 58.8 % ^{39}Ar and an isochron age of 104 ± 42 ka was determined. Sample PK-6 gave a single plateau age of 141 ± 51 ka (81.8 % of ^{39}Ar) with an isochron of 169 ± 16 ka. Sample PK-7 gave a plateau age of 124 ± 4 ka including 74.2 % of the ^{39}Ar . A recommended age of 132 ± 19 ka is given for Prestahnúkur (Table 3), which agrees with the age of McGarvie et al. (2007) within uncertainty (**Table 1**). Sample PK-1 had separable feldspar phenocrysts, which gave two apparent ages of 1073 ± 11 and 2445 ± 11 ka (but see discussion in **section 5.2.2**).

5. DISCUSSION

5.1 Volatile contents in subglacial and subaerial obsidians

Unaltered glass samples gave consistent volatile measurements with several identifiable trends. These subglacial and subaerial samples typically: (1) are low in H₂O (~ 0.1 wt. %) content indicating a degassed magma or alternatively, an original volatile-poor melt; (2) have CO₂ below detection limit of (~ 12 ppm), possibly due to either initial low CO₂ contents or the lower solubility of CO₂ compared to e.g., H₂O in silicate glasses; and (3) have consistent halogen concentrations between samples of a given eruptive unit. These trends exclude samples that suffered post-emplacement modification or alteration (noted in **Tables 1 and 3**). Samples can therefore be separated into those which represent degassed subglacial or subaerial obsidians (identified in **Table 3**) and those which have undergone post-eruptive modification or alteration resulting in obvious hydration or alteration. Results are discussed in detail below.

H₂O and Cl in rhyolite melts are efficiently extracted from the melt during degassing processes (Balconne-Boissard et al., 2010), as hydrophilic Cl will typically partition into a fluid phase (e.g., Dunbar and Kyle, 1992). Despite this, we find no correlation between H₂O and Cl concentrations in the obsidians (**Fig. 3a**). Additionally, there is considerable variability in the measured H₂O content (from nearly anhydrous to ~ 0.7 wt. %). This lack of correlation could indicate a decoupling of magmatic Cl from a fluid phase upon decompression and degassing. In altered and microcrystalline rhyolites, e.g., TJ-98/50, the observed high H₂O and low Cl content, may indicate a loss of halogens with hydration upon fluid-alteration or from secondary mineral formation (Shigley and Brown, 1985; **Fig. 3a, b**) but these samples almost certainly do not reveal any information on primary H₂O melt signatures or degassing efficiency, but rather on post-eruptive modification of the samples themselves. Chlorine and F are roughly correlated (**Fig. 3b**), likely due to the similarity of the behavior of the halogen group elements in rhyolite upon decompression and degassing (i.e., high H₂O-vapor melt partition coefficients; Balconne-Boissard et al., 2010). Prestahnúkur samples have homogenous Cl and F compositions which may attest to the single magma batch, small-

volume nature of the eruption as suggested by McGarvie et al. (2006) but more likely reflects similar efficiency of degassing during eruption of Prestahnúkur rhyolites.

The observed variability in H₂O content may reflect differences in initial water content, variation in degassing efficiency in different eruption settings or differences in pressure at the time of eruption, such as may result from the pressures of the overlying ice-lid. Water contents can be considered in the context of the pressure of the overlying ice for subglacial eruptions where ice thickness estimates exist (Bláhnúkur and Prestahnúkur) using the low pressure solubility data for H₂O in rhyolite of Liu et al. (2005) (**Fig. 3c**). Bláhnúkur glass preserved a water content of 0.69 ± 0.01 wt. % which corresponds to the predicted water content at ~ 40 kbar pressure or ~ 450 m of overlying ice (**Fig. 3c**). This fits well with the estimated minimum overlying ice thickness of 400 m for Bláhnúkur at the time of eruption from the study of Tuffen et al (2002). Prestahnúkur would be predicted to contain ~ 0.9 wt. % H₂O based on eruption under an ice thickness of 700 m (McGarvie et al., 2006) or ~ 60 kbar but actually contains only ~ 0.12 wt. % H₂O, consistent across the three samples measured in this study (**Fig. 3c**). Such low H₂O contents suggest efficient loss of volatiles despite the overlying ice and quenching at atmospheric pressure.

5.2 Assessment of Ar data

Many subglacial glass samples produced plateau or isochron ages (e.g., Bláhnúkur, Hábarmur, Háskerðingur and Prestahnúkur). All new ages are given in the context of all samples including their uncertainty minimum and maximum limits and previous age determinations from McGarvie et al. (2006, 2007) in **Figure 6a**. The former compares with a range of 108 ± 22 to 255 ± 20 ka for Torfajökull obsidians determined here. Specifically, the sample from Hábarmur is the oldest in both the study of McGarvie et al. (2006) and in the current study, yet discrepant by approximately 130 ka (384 ± 20 ka isochron age compared to 255 ± 20 ka plateau age). Both the present study and McGarvie et al. (2006)

chose handpicked, fresh obsidian and used laser step-heating to release gases. Different standard monitor minerals were used however this cannot account for the 130 kyr age difference. The age for Prestahnúkur of 89 ± 24 ka (McGarvie et al. 2007; **Fig. 6a**) overlaps within uncertainty but is at the low end of the age spectrum for the determined ages in this study.

Glass samples that did not yield any geologically meaningful $^{40}\text{Ar}/^{39}\text{Ar}$ age information (TJ/98-50, TJ/98-39, TJ/97-14) had characteristics that may cause disturbances to the Ar-system and therefore inhibit age determination. Such characteristics include: (1) variable release of radiogenic $^{40}\text{Ar}^*$ from different carrier phases due to alteration or highly microcrystalline groundmass (Hábarmur; TJ/97-14, Kaldaklofsjöll; TJ/98-39 and TJ/98-50, respectively); (2) the presence of excess Ar which has been previously observed sequestered in secondary alteration products (see below and Villa and Taddeucci, 1991; Kaldaklofsjöll and Hábarmur); and (3) small amounts of ^{36}Ar and radiogenic $^{40}\text{Ar}^*$ in exceptionally young samples (<10 ka; Hrafninnusker with up to 93% air-derived Ar).

In order to assess sample homogeneity, neutron reactions on Cl, K and Ca during irradiation can be used as indirect measurements of these elements and thus evaluation of their relative homogeneity in each sample. The Cl/K [from $^{38}\text{Ar}/^{39}\text{Ar}$; ($^{37}\text{Cl}(\text{n},\gamma)^{38}\text{Cl}(\beta^-)^{38}\text{Ar}$ and $^{39}\text{K}(\text{n},\text{p})^{39}\text{Ar}$) and Ca/K [from $^{37}\text{Ar}/^{39}\text{Ar}$; ($^{40}\text{Ca}(\text{n},\alpha)^{37}\text{Ar}$)] systematics of each sample was qualitatively assessed. Altered (e.g., TJ/97-14, TJ/98-50) and microcrystalline samples (e.g., TJ/98-39) yielded highly variable $^{38}\text{Ar}/^{39}\text{Ar}$ and $^{37}\text{Ar}/^{39}\text{Ar}$ release patterns, indicating the presence of Cl, Ca, and K in multiple mineral phases. The samples are not pure glass separates and therefore uniform release of K, Ca and Cl would not be anticipated. Other glass samples revealed homogenous Cl/K and Ca/K release patterns, particularly Hrafninnusker (samples HSK-12 and HSK-32). Argon data confirms that glass samples are homogenous with respect to K, Ca and Cl distribution. Note that Cl isn't assessed quantitatively by this method due to a minimized production of ^{38}Ar (shielded irradiation) and thus relatively large uncertainties in the determination of Cl abundance.

5.2.1 Sub-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$, mass-fractionation and eruption at non-atmospheric pressures

Despite plateau and isochron ages that agree within error, some subglacial rhyolites from both Torfajökull and Prestahnúkur give apparent sub-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ intercept (e.g., sample PK-6, **Fig. 5c**). This may simply indicate poorly-constrained data (e.g., in the case of **Fig. 5b**) but it could also suggest that some samples contain a trapped Ar component with $^{40}\text{Ar}/^{36}\text{Ar}$ below that of modern air (e.g., **Fig. 5c**). This would necessitate a different correction for trapped Ar. In the samples studied here, the sub-atmospheric values are not sufficiently consistent to rigorously define a different correction factor; however, they do raise interesting questions about the role that magma-ice interaction and variable eruption cavity pressures may have on age determination. Sub-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ values have previously been reported in young volcanic rocks (see Krummenacher, 1970; Kaneoka, 1980, Matsumoto and Kobayashi, 1995), and have been attributed to excess ^{36}Ar . Volcanic rocks can capture and incorporate an isotopically fractionated light ‘atmospheric’ Ar, which can be introduced via groundwater or from surrounding wall-rock, towards the top of a magma chamber (Kaneoka, 1980; Matsumoto et al., 1989). More recently, Morgan et al. (2009) suggested rapid quenching of glass could prevent complete atmospheric equilibration, thus giving low, fractionated $^{40}\text{Ar}/^{36}\text{Ar}$. In the present study, investigating mass fractionation with $^{38}\text{Ar}/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios is limited by the uncertainty on corrections for reactor-induced production of ^{38}Ar (though the irradiation was shielded to minimize this, any reactor-produced ^{38}Ar will dominate over natural, low abundance ^{38}Ar in these samples). Argon has a higher solubility in air and water relative to rhyolite melt, however, dissolved ^{36}Ar may preferentially diffuse back into the magma upon degassing due to the enhanced diffusivity of ^{36}Ar compared to ^{40}Ar (cf. Young et al., 2002). Therefore if subglacial obsidians quenched with melt water or air prior to achieving complete equilibration, mass fractionation could occur and low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios would result. Identification of physical and chemical processes that influence the $^{40}\text{Ar}/^{36}\text{Ar}$ trapped composition of subglacial eruption products is important for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of young samples and is an area that requires further

work.

5.2.2 Erroneous apparent ages in feldspar from subglacial rocks

Crystal contents in many of these samples are either small ($\ll 10\%$) or absent. Where present in sufficient quantity to separate and analyze we attempted step-heating experiments on plagioclase separates. These samples include Hábarmur (TJ/98-39), Háskerðingur (TJ/98-6) and Prestahnúkur (PK-1). The determined ‘apparent ages’ are shown in **Table 3** and **Figure 6b** in the context of the corresponding glass age for each sample. In each case, feldspar ages are older than glass, with differences between glass and feldspar ages (Δ age, **Fig. 6b**) ranging from ~ 80 ka at Bláhnúkur to ~ 900 to 2000 ka at Prestahnúkur. These erroneously old ages could result from either incorporation of an older xenocrystic crystal component or the presence of excess Ar in the feldspar, though no evidence for xenocrysts is seen and a feldspar population comprised of entirely xenocrysts is highly unlikely. Excess Ar, however, may be problematic. Argon is generally thought to be incompatible (K_D mineral/melt $\ll 1$; Kelley, 2002) but some workers (Clay et al. 2010; Baxter et al., 2010 and references therein) have suggested that uptake of Ar in the outermost portions (100s nm to 10s microns) of mineral surfaces may be significant (e.g., 1000’s ppm concentrations). Incorporation of excess Ar within these surfaces could account for the older apparent ages. This phenomenon of excess Ar present in feldspars is typically not noted for subaerial eruption settings (cf. Clay et al., 2011; Arico Formation, Tenerife) and indeed the opposite has been observed; excess ^{40}Ar sequestered in the glass phase whilst feldspar yield accurate eruption ages. Subglacial settings are arguably more complex. Putting the ages into the context of their eruption settings, the largest Δ age coincides with the thickest ice estimate (Prestahnúkur; **Fig. 6b**) while the smallest Δ age coincides with a lower ice estimate (Bláhnúkur; **Fig. 6b**). Unfortunately, there is currently no ice thickness estimate for Háskerðingur (intermediate Δ age of ~ 600 ka) and no separable feldspars from Hábarmur to investigate this link further. These preliminary data are not enough to quantitatively suggest a link between ice thickness and the observed elevated excess Ar concentrations in feldspar but the observation raises

interesting questions regarding the consequences of the complexity of subglacial eruptions for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. Multiple analyses of glass and feldspar (and perhaps other phases) across eruption products of varying ages and subglacial environments would be valuable in investigating this issue.

5.2.3 Application of the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique to volcano-ice interactions: Current limitations and future outlook

One of the driving forces behind the application of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer to volcanic glass is to constrain the timing and tempo of glacio-volcanism and reconstruction of paleo-climate models in the recent past. Tuya height can be used as a constraint on the minimum thickness of the syn-eruptive ice sheet and obtaining $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the tuyas gives additional value to this palaeo-environmental indicator by linking *minimum* ice sheet thickness to a particular location at specific time in the past (see Owens et al., 2012). This is particularly useful in Iceland, where obsidian is a dominant K-bearing phase of recent eruptions and crystal-poor eruptive products are common (e.g., Prestahnúkur) and often have low-K contents. Using the ice thickness estimates of Tuffen et al. (2001) and McGarvie et al. (2007), $^{40}\text{Ar}/^{39}\text{Ar}$ ages for Torfajökull and Prestahnúkur should theoretically be able to anchor these ice thickness estimates at a specific point in the past [i.e., emplacement of the Bláhnúkur rhyolite under ice of ~ 450 m (Tuffen et al., 2001) occurred at 108 ± 22 ka]. When placed in a greater climatostratigraphic context as shown in **Figure 6c**, a relative temperature range corresponding to ice thickness should be able to be estimated. For example Prestahnúkur erupted under an estimated 700 m ice thickness based on field observations (McGarvie et al., 2007). The age of Prestahnúkur (132 ± 19 ka) determined here corresponds to temperatures spanning from -2 °C to $+4$ °C relative to current temperatures. The current limitations of this approach however, are clear: uncertainties on ages and variations between sample populations (and different studies) may limit the precision to which the timing and tempo of volcanic events can be constrained (see range on **Fig. 6c**). Hence, greater precision ($\sim \pm 2$ -5 ka; **Figure 6c**) is required for young samples in order for meaningful interpretations of past climate. Nevertheless, using $^{40}\text{Ar}/^{39}\text{Ar}$ ages to

pinpoint past climatic conditions remains a promising application for this geochronometer, it simply requires improved understanding of the complex interactions between erupting magma and ice, continued investigation of the disturbances to the Ar system in subglacial settings and perhaps more important, greater precision on $^{40}\text{Ar}/^{39}\text{Ar}$ ages of obsidians.

6. CONCLUSIONS

Volatile contents and $^{40}\text{Ar}/^{39}\text{Ar}$ ages for subglacial obsidians at Torfajökull and Prestahnúkur have been determined: 108 ± 22 ka (Bláhnúkur), 255 ± 20 ka (Hábarmur), 236 ± 7 ka (Háskerðingur) and 132 ± 19 ka (Prestahnúkur). In other samples where ages could not be determined, disturbances to the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer were correlated with a heterogeneous distribution of volatiles in glass and linked to hydration (e.g., Kaldaklofsjöll), mild alteration (e.g., Hábarmur) and alteration and/or recrystallization of glass (e.g., Bláhnúkur). Icelandic rhyolite glasses often contain trapped Ar with a sub-atmospheric to atmospheric signature. Sub-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ in the glass is attributed to rapid quenching prior to equilibration, equilibration with an Ar reservoir with non-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ signature, or diffusion of ^{36}Ar into the melt upon quenching at pressure greater than atmospheric. Volatile contents suggest that most subglacial and subaerial samples are degassed and quenched at ~ 1 bar. Bláhnúkur obsidian however, preserves elevated water contents suggesting quenching at ~ 40 kbar or under ~ 450 m of ice, which is consistent with previous field studies. Measured water contents in subglacial glass can therefore provide information on ice thickness at the time of eruption. Our observations indicate that fresh, unaltered, subglacially erupted glasses are appropriate candidates for the application of the $^{40}\text{Ar}/^{39}\text{Ar}$ chronometer, despite the complexities of dynamic volcano-ice interactions, however co-existing feldspars in subglacial settings may suffer from excess Ar. Caution is suggested when placing such ages in the context of glacio-volcanic reconstruction of paleo-climate in the recent past, however, until improvements are made towards reducing $^{40}\text{Ar}/^{39}\text{Ar}$ age-uncertainties $^{40}\text{Ar}/^{39}\text{Ar}$.

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FIGURE CAPTIONS

Figure 1 (a) Map of Iceland showing the locations of field sites in this study: Torfajökull volcanic center (seen in detail in b) and Prestahnúkur (seen in detail in c). **(b)** The Torfajökull central volcano showing the distribution of rhyolite eruption products: Bláhnúkur (TJ/98-39 and TJ/98-40); Kaldaklofsjöll (TJ/98-50); Haskerðingur (TJ/98-6); Hábarmur (TJ/97-14 and TJ/97-15); and the post-glacial deposits, Hrafninnusker (HSK-12 and HSK-32). **(c)** Prestahnúkur small volume rhyolite edifice showing the location of samples PK-1, PK-6 and PK-7 by elevation in the upper and lower tier (described in detail by McGarvie et al., 2006).

Figure 2 (a) Whole-rock total-alkali vs. silica content of Torfajökull and Prestahnúkur rhyolites. Totals were re-calculated to 100 % prior to plotting according to Le Bas et al. (1986). Whole rock analyses were measured by XRF (OU). **(b)** Rhyolite classification of samples after McDonald et al. (1974). Field abbreviations: PB, picro-basalt; B, basalt; A, andesite; D, dacite; Bas, basanite; F, foidite; PhT, phonotephrite; Tph, tephriphonolite; Ph, phonolite; TrA, trachyandesite; TrD, trachydacite; Tr, trachyte.

Figure 3 Water, fluorine and chlorine concentrations in all samples as determined by nanoSIMS 50L measurements (OU). **(a)** Cl (ppm) vs. H₂O (wt. %) concentrations in all samples. **(b)** Chlorine (ppm) vs. F (ppm) concentrations in all samples. Grey shaded areas represent volatile contents found in typical degassed obsidian. **(c)** Predicted water content as a function of ice thickness and pressure using the low-pressure solubility study of Liu et al. (2005). Note Bláhnúkur (TJ/98-40) H₂O content corresponds to a pressure of ~40 kbar and an ice thickness of ~450 m at the time of eruption.

Figure 4 Step-heating spectra for all Icelandic obsidian samples by eruption unit. Plateau ages are denoted with a thick dashed line and error bars are shown with vertical lines. **(a)** and **(b)** Háskerðingur (TJ/98-6); **(c)** and **(d)** Hábarmur (TJ/97-15); **(e)** and **(f)** Bláhnúkur (TJ/98-40) and **(g-k)** Prestahnúkur rhyolites (PK-1, PK-6 and PK-7). See text for discussion, Table 4 for summary information and the Supplementary Materials for full data set.

Figure 5 Inverse isochron for selected step-heating experiments given in Figure 4 by eruption unit. **(a-c)** Prestahnúkur rhyolites (PK-1, PK-6 and PK-7) and **(d)** Háskerðingur (TJ/98-6). Apparent age and $^{40}\text{Ar}/^{36}\text{Ar}$ intercept is given in each panel by sample. Modern $^{36}\text{Ar}/^{40}\text{Ar}$ composition of the atmosphere plots at 0.00338 on the y-axis as a grey star. See text for discussion, **Table 4** for summary information and the Supplementary Materials for full data set.

Figure 6 (a) Age distribution of obsidians in this study. The minimum and maximum ages for Torfajökull eruptive products from McGarvie et al. (2006) are given by dashed grey lines. Recommended ages as calculated for this study for each eruption are shown by dark red point. Uncertainty given by error bars are 1σ . **(b)** Age distribution of glass and corresponding feldspar by eruption unit. The Δ age for each sample is given and the approximate ice thickness for each sample where available (in grey). **(c)** Recommended ages for Torfajökull and Prestahnúkur determined in this study in context of the paleo-temperature curve for the last 450 ka based on data set from the Vostok ice-core (Petit et al., 1999) and corresponding marine isotope record for the $\delta^{18}\text{O}$ curve (Martinsen et al., 1987). Sample symbols given in legend. Glacial (Weichselian, Saalian) and interglacial (Eemian) stages labeled for reference. Note the required precision ($\sim \pm 2\text{-}5$ ka) necessary for $^{40}\text{Ar}/^{39}\text{Ar}$ ages to yield meaningful information on past climate (see discussion section 5.2.3).

TABLES

Table 1. Sample locations, descriptions and ages from previous studies (see foot note for references).

Sample	Location	Brief Description	Age, ka	$\pm (1\sigma)$
<i>Torfajökull</i>				
TJ/97-15; TJ/97-14	Hábarmur	TJ/97-15 is aphyric rhyolite obsidian. TJ/97-14 is hydrothermally altered glass-bearing rhyolite with microcrystalline groundmass	384*	20
TJ/98-39; TJ/98-40	Bláhnúkur	Small-volume subglacial, effusively erupted rhyolite. TJ/98-40 is a rhyolite obsidian vitrophyre, with a low crystal content ($\ll 10\%$). TJ/98-39 is a glass-bearing microcrystalline rhyolite with mildly altered groundmass		
TJ/98-50	Kaldaklofsfjöll	Subglacially erupted glass-bearing phenocryst-bearing rhyolite with altered groundmass		
TJ/98-6	Háskerðingur	Subglacial dome eruption of rhyolite vitrophyre with a low crystal content ($\ll 10\%$)		
HSK-12, HSK-32	Hrafninnusker	Subaerial, effusively erupted aphyric rhyolite	$<10,000^\dagger$	
<i>Prestahnúkur</i>				
PK-1, PK-6 and		Subglacial, effusively erupted rhyolite	89 ‡	24

*Reference: *McGarvie et al., 2006; †McGarvie, 1984; ‡McGarvie et al., 2007. For consistency, descriptive terms for samples follow the guidelines of the IUGS Subcommittee on the Systematics of Igneous Rocks (Le Maitre, 2002).*

Table 2. XRF whole rock major and minor element analyses (OU) for Torfajökull and Prestahnúkur rhyolites. See section 2.1.2 for full analytical details including incorporation of standards.

Sample	TJ/97-14	TJ/97-15	TJ/98-6	TJ/98-39	TJ/98-40	TJ/98-50	PK-1	PK-6	PK-7	*PK-7	† HSK-12	† HSK-32
SiO ₂	73.3	76.2	72.1	69.6	69.3	74.5	75.8	76.4	73.0	76.6	73.3	71.7
TiO ₂	0.31	0.13	0.33	0.29	0.29	0.28	0.12	0.13	0.31	0.12	0.21	0.23
Al ₂ O ₃	10.4	12.0	11.5	13.9	13.8	8.50	11.8	12.0	10.3	12.1	12.6	14.1
Fe ₂ O ₃ T	5.06	1.77	4.82	3.35	3.37	6.43	1.60	1.75	5.06	1.73	3.13	2.70
MnO	0.11	0.05	0.13	0.09	0.09	0.17	0.05	0.05	0.13	0.05	0.09	0.08
MgO	0.07	0.07	0.09	0.30	0.34	0.08	0.07	0.07	0.08	0.02	0.04	0.11
CaO	0.18	1.04	0.46	0.97	1.05	0.25	0.96	1.03	0.32	1.04	0.38	0.67
Na ₂ O	4.96	4.36	5.84	5.57	5.69	3.77	4.31	4.37	5.43	4.40	5.04	5.28
K ₂ O	4.48	3.21	4.26	4.25	4.20	4.14	3.34	3.21	4.43	3.30	4.26	4.23
P ₂ O ₅	0.01	0.01	0.01	0.03	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.01
LOI	0.26	0.07	0.21	0.03	1.21	1.22	0.27	0.27	0.30	0.36	--	--
Total	99.2	98.9	99.8	98.4	99.3	99.4	98.4	99.3	99.4	99.8	99.0	99.1
<i>Trace Elements</i>												
Rb	113	115	105	106	106	116	84	80	82	79	123	114
Sr	bd	bd	25	60	56	bd	69	78	79	77	11	45
Y	93	157	146	89	87	181	94	105	107	110	128	100
Zr	1622	1590	1436	831	821	1693	204	245	259	254	1036	706
Nb	211	208	201	122	122	247	56	63	64	66	171	143
Ba	103	115	577	478	464	271	631	637	629	628	185	399
Pb	11	12	11	10	bd	13	bd	bd	bd	bd	22	18
Th	20	21	19	17	19	25	12	14	13	13	25	22
Ni	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	16	12
Zn	315	320	300	116	129	314	100	119	121	116	251	168
Ga	41	41	39	32	31	42	22	23	23	22	bd	bd
<i>bd, below detection. Italicized values represent poor analysis (see section 4.1)</i>												
<i>Typical precision on XRF analyses 0.2 -0.7 wt. %</i>												
<i>† Values from McGarvie et al., 2007; *Values from McGarvie et al., 1990</i>												

Table 3. Volatile concentrations for Torfajökull and Prestahnúkur rhyolites as determined by Cameca NanoSIMS 50L (OU). All concentrations are reported as ppm except water which is given in weight %.

Unit	H ₂ O	±	CO ₂	±	F	±	Cl	±	S	±	Commentt	n
<i>Bláhnúkur</i>												
TJ/98-40	0.69	0.01	nd		1690	40	2000	120	6	1	<i>p</i>	6
TJ/98-39	< 0.1		< 5		80	5	nd		nd		<i>mc, het</i>	5
<i>Haskerðingur</i>												
TJ/98-6	0.08	0.01	nd		1650	90	1300	80	18	1	<i>p</i>	8
<i>Kaldaklofsjöll</i>												
TJ/98-50	0.40	0.08	640	110	250	40	30	10	120	7	<i>pem, het</i>	5
<i>Hábarmur</i>												
TJ/97-14	0.13	0.03	7800	2200	1320	160	290	100	30	5	<i>pem, het</i>	8
TJ/97-15	0.09	0.01	nd		1780	40	1620	50	45	1	<i>p</i>	8
<i>Hraftinnusker</i>												
HSK-12	0.09	0.01	nd		1740	10	1590	20	45	5	<i>p</i>	6
HSK-32	0.08	0.01	nd		1600	30	1760	80	10	3	<i>p</i>	4
<i>Prestahnúkur</i>												
PK-1	0.12	0.01	nd		840	10	460	10	nd		<i>p</i>	6
PK-6	0.13	0.01	nd		880	10	430	10	nd		<i>p</i>	6
PK-7	0.11	0.01	nd		900	10	450	20	nd		<i>p</i>	6
<i>p, taken as residual (degassed), unaltered; pem = post-eruption modification; het = heterogeneous; mc = microcrystalline; n = number taken in average; bd = below detection</i>												

Table 4. Summary of new ages for Torfajökull and Prestahnúkur rhyolites. Errors are 2σ . Refer to section 3.2 for full analytical details. Apparent ages in parentheses indicate altered sample which may have been affected by excess Ar. Weighted mean ages given in text and full data set given in **the Supplementary Material** .

	Plateau (ka), 1σ uncertainty	MSWD	Isochron (ka), 1σ uncertainty	MSWD	$^{40}\text{Ar}/^{36}\text{Ar}$ (intercept)
<i>Prestahnukur</i>					
PK-1 , Glass	123 ± 16	0.35	NA		
	136 ± 10	0.35	160 ± 16	16	254 ± 490
	135 ± 14	0.038	104 ± 42	4.5	431 ± 100
PK-6, Glass	141 ± 51	0.054	169 ± 16	304	58 ± 120
PK-7, Glass	124 ± 4	0.44	NA		
<i>Prestahnukur Age:</i>	<i>132 ± 19</i>				
<i>Torfajokull</i>					
TJ-98/6, Glass	232.4 ± 5.7	0.31	216 ± 13	0.91	240 ± 28
	239.8 ± 7.0	0.92	190 ± 82	0.98	475 ± 220
<i>Haskerdingur Age:</i>	<i>236 ± 7</i>				
TJ-97/15, Glass	260 ± 24	2.1			
	249 ± 13	1.04			
<i>Habamur Age:</i>	<i>255 ± 20</i>				
TJ-98/40, Glass	119 ± 22	0.92			
	98 ± 20	0.019			
<i>Blahnukur Age:</i>	<i>108 ± 22</i>				
*Feldspar Apparent Ages					
PK-1, Feldspar	(1080 ± 300)		(1073 ± 11)	10.5	13 ± 130
	NA		(2445 ± 11)	24.7	
TJ-98/6, Feldspar	NA		(827.9 ± 8.4)	25	95 ± 140
TJ-98/39, Feldspar	(189 ± 34)	2	NA		

**All feldspar ages excluded, due to presence of excess Ar and/or potential xenocrystic component (see text for discussion)*

ELECTRONIC SUPPLEMENTARY MATERIAL

Electronic Supplementary Material 1. Sample descriptions and characterization.

Electronic Supplementary Material 2. Complete $^{40}\text{Ar}/^{39}\text{Ar}$ age data for 30 step-heating experiments of Torfajökull and Prestahnúkur rhyolite glass. ^{40}Ar , ^{39}Ar , ^{38}Ar , ^{37}Ar and ^{36}Ar are in 10^{-10} cc-STP g^{-1} . Ages of steps are in Ma and incorporate a 0.5 % error in the J-value. Refer to text for discussion.