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# Pollution from the 2014-15 Bárðarbunga eruption monitored by snow cores from the Vatnajökull glacier, Iceland

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## ABSTRACT

The chemical composition of Icelandic rain and snow is dominated by marine aerosols, however human and volcanic activity can also affect these compositions. The six month long 2014-15 Bárðarbunga volcanic eruption was the largest in Iceland for more than 200 years and it released into the atmosphere an average of 60 kt/day $SO_2$, 30 kt/day $CO_2$, 500 t/day HCl and 280 t/day HF. To study the effect of this eruption on the winter precipitation, snow cores were collected from the Vatnajökull glacier and the highlands northeast of the glacier. In addition to 29 bulk snow cores from that precipitated from September, 2014 until March, 2015, two cores were sampled in 21 and 44 increments to quantify the spatial and time evolution of the chemical composition of the snow.

The pH and chemical compositions of melted snow samples indicate that snow has been affected by the volcanic gases emitted during the Bárðarbunga eruption. The pH of the melted bulk snow cores ranged from 4.41 to 5.64 with an average value of 5.01. This is four times greater $H^+$ activity than pure water saturated with the atmospheric $CO_2$. The highest concentrations of volatiles in the snow cores were found close to the eruption site as predicted from CALPUFF $SO_2$ gas dispersion quality model. The anion concentrations ($SO_4$, Cl, and F) were higher and the pH was lower compared to equivalent snow samples collected during 1997−2006 from the unpolluted Icelandic Langjökull glacier. Higher $SO_4$ and Cl concentrations in the snow compared with the unpolluted rainwater of marine origin confirms the addition of a non−seawater $SO_4$ and Cl. The $\delta^{34}S$ isotopic composition confirms that the sulphur addition is of volcanic aerosol origin.

The chemical evolution of the snow with depth reflects changes in the lava effusion and gas emission rates. Those rates were the highest at the early stage of the eruption. Snow that fell during that time, represented by samples from the deepest part of the snow cores, had the lowest pH and highest concentrations of $SO_4$, F, Cl and metals, compared with snow that fell later in the winter. Also the Al concentration, did exceed World Health Organisation drinking water standard of 3.7 µmol/kg in the lower part of the snow core closest to the eruption site.

Collected snow represents the precipitation that fell during the eruption period. Nevertheless, only minor environmental impacts are evident in the snow due to its interaction with the volcanic aerosol gases. In addition, the microbial communities identified in the snow that fell during the eruption were similar to those found in snow from other parts of the Arctic, confirming an insignificant impact of this eruption on the snow microecology.

## 1. INTRODUCTION

Volcanic eruptions pose environmental risks and monitoring of volcanic activities is a major task for the geoscientific community. Volcanic hazards include degassing, volcanic gas dispersion, acid rain, pollution of surface waters, potential volcanic ash production and glacial outburst floods. These hazards have been previously investigated and used for civil- and environmental protection development in vicinities of the active volcanoes (e.g., Aiuppa, 2009; Aiuppa et al., 2006, 2007, Bagnato et al., 2013; Björnsson, 2003; Bobrowski et al., 2007; Calabrese et al., 2011; Cuoco et al., 2013; D'Alessandro et al., 2013; Delmelle, 2003; Delmelle et al., 2002; Delmelle et al., 2007; Delmelle et al., 2015;  Flaathen and Gislason, 2007; Floor et al., 2011; Galeczka et al., 2014a; Gislason et al., 2002; 2011; Gudmundsson et al., 1997, 2008; Jones et al., 2011; Kristmannsdóttir et al., 1999; Moune et al., 2006; Menard et al., 2014; Oppenheimer 2003; Roberts et al., 2000; Russell et al., 2006, 2010; Snorrason et al., 2002; Stefánsdóttir and Gislason, 2005; Thordarson and Self, 2003; Thordarson and Larsen, 2007; Tómasson, 1996).

The 2014-2015 Bárðarbunga eruption (Galeczka et al. 2016; Gislason et al., 2015; Gauthier et al. 2016; Gudmundsson et al., 2016; Sigmundsson et al, 2015; Stefánsson et al. 2017a) brought the possible effects of sustained eruptive degassing in the troposphere to the world's attention. Eruption vents during the 2014-15 Bárðarbunga eruption were located on the outwash plains of the Dyngjujökull glacier, on the historical Holuhraun lava that erupted between 1794 and 1864 (Fig. 1; Hartley and Thordarson, 2013). In this manuscript, the 2014-15 lava field will be referred to as the Holuhraun lava. The lava produced during this activity covered an area of 84.1 ± 0.6 $km^2$ and the volume was estimated to be 1.6 ± 0.3 $km^3$ (Gislason et al. 2015; Gudmundsson et al. 2016) making it the largest eruption in Iceland since the 1783-84 Laki eruption (Thordarson and Larsen, 2007). Ground based and satellite remote sensing presented by Arason et al., (2015) indicate that substantial $SO_2$ was continuously emitted to the troposphere during the eruption with plumes reaching 1–3 km in height. The total gas emissions to the atmosphere during the Bárðarbunga eruption were 11.2 Mt of $SO_2$, 6 Mt of $CO_2$, 0.1 Mt of HCl, and 0.05 Mt HF (Gislason et al., 2015; Stefánsson et al. 2017a). For comparison, global volcanic $SO_2$ emissions from all the Earth's volcanoes are on the order of 7.5-10.5 Mt (Halmer et al., 2002). The 2014-15 Bárðarbunga eruption gas emission rate caused anomalously high atmospheric $SO_2$ concentrations in Iceland and several locations in Europe (Gislason et al., 2015; Schmidt et al., 2015) with an average emission rates of 62 kt/day during the eruption and up to 133 kt/day during September 2014 (calculated using petrologic method and DOAS measurements; Gislason, 2015; IMO, 2017). Similar $SO_2$ fluxes were reported by Gauthier and co-workers (2016) and equalled 97 kt/day. These high emissions affected rain and snow chemical composition all over Iceland (Gislason et al., 2015; Stefánsson et al., 2017a).

During winter and/or in cold areas, gasses and aerosols sourced by natural and manmade activities are transported and may accumulate in snow. Globally, aerosols are sourced from oceans (1000 Mt/yr), soils or continental surface (so called continental aerosols; 100-1000 Mt/yr), and anthropogenic and volcanic activities (Shaw, 1989). A large portion of the annual precipitation in Iceland falls as snow. Volcanic activity considerably affects the snow chemical composition, mainly via deposition of volcanic ash particles and gaseous aerosols. Volcanic aerosols are abundant in the vicinity of erupting volcanoes, and some may be dispersed around the globe. These aerosols form during condensation of gases and their composition might be modified due various processes e.g., coagulation, evaporation, and interaction with other gases, organic compounds, volatiles, and other particles (e.g., IPCC, 1994; Jacobson, 1998; Seinfeld and Pandis, 2006). Snow has been shown to incorporate aerosols and gases during snowfall, (Budhavant et al., 2014; Magono 1979; Paramonov et al., 2011). Notably, below the clouds, aerosol particles tend to be scavenged on the rim of ice crystals (Pruppacher and Klett, 1997). Aerosols can be also scavenged directly by cloud droplets (e.g., Jacobson, 1998; Seinfeld and Pandis, 2006). Because of the shapes, densities and growth mechanisms of snow crystals, the removal of aerosols from the atmosphere by snow is far more efficient than by rain based on equal equivalent water content of the precipitation (Andronache, 2009; Graedel and Franey, 1975; Jylha, 2000; Kyro et al., 2009). Aerosols scavenged by snow will dissolve during snowmelt and the trapped, often acidic gases will lower the pH of the meltwater (e.g. Flaatheen and Gislason, 2007; Galeczka et al., 2016).

As indicated by laboratory and field experiments, 50–80% of the pollutants in snow (including protons as a source of acidity) are released with the first 30% of the meltwater and this first meltwater fraction may contain more than five times the average snowpack ionic concentrations (Johannessen and Henriksen, 1978). Melting of 10% of the 1987–88 winter snowpack on the Vatnajökull glacier produced meltwater more than one pH unit lower than the original snowpack's pH (Gislason, 1990). As shown earlier in northern North America, Scandinavia and Britain, accumulation of polluted snow during the winter and subsequent spring melt caused acidification, decreasing local lake and stream pH by 1 to 1.5 log units (Davies 1989; Tranter, 1989; Wigington, 1989). An increase in toxic element concentrations (e.g., Pb) have been recorded in Greenland and Antarctic snow and ice in response to the atmospheric anthropogenic emissions (Bautron et al., 1991, 1998, Candelone et al., 1995; Hong et al., 1994, 1996). Snow also accumulates volcanic pollutants such as fluoride and aluminium (e.g., Flaathen and Gislason, 2007; Galeczka et al., 2016; Moune et al., 2006). Melting of such polluted snow, therefore, leads to the release of these toxic elements to aquifers and surface waters (Flaathen and Gislason, 2007).

In this study we report on the chemical, isotopical and microbiological composition of snow accumulated during the 2014-15 Bárðarbunga volcanic eruption on the Vatnajökull glacier and the highlands NE of the glacier. We studied the spatial and temporal evolution of the chemical composition of the snow, as it reflects fluctuations in the eruption effusion and emission rates, wind direction and distance from the eruption source. Sulphur isotopes were applied to determine the source(s) and reactions of sulphur in these systems (e.g., Gunnarsson-Robin et al., 2017; Herut et al. 1995). In addition we analysed the snow microbial community composition using high-throughput sequencing. The purpose of this communication is to report the results of this study, which further illuminates the effects of the emission of volcanic gases on precipitated snow.

## 2. GEOGRAPHICAL AND GEOLOGICAL SETTINGS

About 11% of Iceland is covered by glaciers; their regional distribution is dictated by topography and precipitation, which are dominated by prevailing southerly winds (Björnsson and Pálsson, 2008). The glaciers contain about 3,600 km$^3$ of water, which is equal to about 200 years of winter precipitation on these glaciers, based on the 2014-15 snow mass balance measurements (Pálsson et al., 2015). The Vatnajökull glacier has around 30 outlet glaciers flowing from the ice cap and feeding some of the largest rivers in Iceland, including the Jökulsá á Fjöllum, which was affected by the 2014-15 Bárðarbunga eruption (Galeczka et al., 2016; Gislason et al., 2015). These rivers transport dissolved and suspended material to the oceans, affecting the elemental budget of the coastal waters (Eiriksdottir et al., 2015; 2017). The Vatnajökull is located on a highland plateau, 600-800 m a.s.l. with 88% of its base above 600 m and only 20% exceeding 1100 m, which is the glaciations limit for southern Iceland (Björnsson and Pálsson, 2008). It is located far from anthropogenic aerosols sources (Gislason, 1990), thus changes in chemical constituents in the snow are largely influenced by volcanic inputs if present.

About 60% of the surface underneath Vatnajökull glacier contains active volcanoes (Björnsson and Einarsson, 1990; Björnsson and Pálsson, 2008). There are several central volcanoes beneath the glacier, including Gjálp that erupted in 1996, Grímsvötn that erupted in 1998, 2004 and 2011, Bárðarbunga whose eruption ended in February 2015, and Hamarinn, whose cauldrons were the source of a modest flood during 2011 (Galeczka et al. 2014a; Gislason et al., 2002, 2015; Gudmundsson and Högnadóttir, 2007; Gudmundsson et al., 1997; Hannesdóttir, 2011; Hreinsdóttir et al. 2014; IMO, 2017; Sigmundsson et al., 2015). Large glacial floods are common from geothermal and volcanic areas underneath the Vatnajökull glacier (Björnsson, 1998, 2003; Björnsson and Einarsson, 1990; Gislason et al., 2002, Stefánsdóttir and Gislason 2005).

## 3. CHEMICAL COMPOSITION OF ICELANDIC RAIN AND SNOW

The Icelandic rain water and snow is characterized with Na/Cl, K/Cl, Mg/Cl and Sr/Cl ratios close to the corresponding oceanic ratios (Bruland, 1983) indicating a primary marine origin of these ions (Gislason, 1990; Gislason et al., 1996). The solute concentration in Icelandic precipitation decreases with increasing distance from the Atlantic Ocean indicating sea-spray as its principal source (Gislason and Eugster, 1987b; Gislason, 1993; Sigurdsson and Einarsson, 1988). The solute concentration of rainwater is higher in the winter than during the summer (Gislason and Eugster 1987b; Gislason, 1993). This can be attributed to a higher average winter wind speed and by the fact that aerosol removal by snow is more efficient than by rain (Graedel and Franey, 1975). The average pH of integrated monthly samples of precipitation in southwestern Iceland from 1958 to 1981 presented by Gislason et al. (1996) was 5.4. More recent analyses (2008–2012) indicate that the average annual pH of rain ranged from 5.33 to 5.97 (Eiriksdottir et al., 2014a,b). For comparison, the pH of pure water saturated with atmospheric $CO_2$ (395 ppmv; Keeling and Trans, 2016) at 25 °C equals to 5.56. Precipitation composition for the past several decades was reviewed in Stefánsson et al. (2017a).

The average, maximum and minimum pH, conductivity and element concentrations of uncontaminated winter Langjökull snow samples collected annually during 1997 to 2006 are shown in Table 1 (data taken from Gislason et al., 2000; Eiriksdottir, 2008). In this study Langjökull snow will be used as reference snow for comparison with the 2014-2015 Vatnajökull snow samples collected in this study. In total, 30 snow samples were collected from 1997 to 2006: one sample during 1997 and 1998, two samples each year during 1999-2001 and three samples annually from

2002 to 2006. Similar to the cores collected in the present study, each sample represents the bulk average winter precipitation (September to March/April) at the sampling location. Note however, the geographical and geological settings of these samples are somewhat distinct from those of the present study (Fig. 1). The pH of the Langjökull snow samples ranged from 5.25-6.72 (average pH of 5.74). The average concentrations of major components were lower than those measured in rainwater collected closer to the Atlantic ocean as described above. The Vatnajökull snow samples collected during 1988 by Gislason (1990) had pH ranging from 5.45 to 5.91 (at room temperature) and concentrations of 7.61–22.1 for Na, 0.13–1.41 for K, 0.13–2.13 for Na, 0.29–2.22 for Mg, 3.66–25.6 for Cl, 0.44–4.18 for $SO_4$, and 1.64–4.10 for $HCO_3$ (all in µmol/kg) which is mainly $CO_2$ added during and after melting the snow samples.

Precipitation collected from monitoring stations all over Iceland during the Bárðarbunga eruption (Gislason et al. 2015; Stefánsson et al. 2017a) reveals that this eruption had major effect on the precipitation composition over an area of 100,000 km$^2$ with the majority of the $SO_4$ and F originating from volcanic gas emissions. In contrast to cations, which were relatively unaffected by this eruption, the concentrations of F, and $SO_4$ were about 20 and 3 times higher, respectively, compared to corresponding pre-eruption and recent Icelandic eruption samples (Stefánsson et al., 2017a).

## 4. METHODS

### 4.1. Snow sampling

Most of the sampling locations on Vatnajökull glacier (Fig. 1) have been chosen to match the locations of the annual snow balance measurements performed by the Institute of Earth Sciences, University of Iceland and the Landsvirkjun National Power Company (e.g. Björnsson and Pálsson, 2008; Pálsson et al., 2015). Samples T03, T05, and T08 were collected from the Tungnaárjökull glacier; samples D01, D02, D05, D07, D08, and D12 from the Dyngjujökull glacier; samples B09, B11, B13, B15, and BUDS from the Brúarjökull glacier; samples G01, G04, and BOR were collected from close to the Grímsvötn subglacial volcano. The M01, M02, and M03 samples were taken from the Maríutungur area (see Fig. 1). Names for samples collected outside the Vatnajökull glacier were taken from the geographical landmarks close to the sampling locations (e.g., Hornbrynja, Sauðahnjúkar, Kiðufell mountains).

After snow coring, the snow was collected into acid washed (1 M HCl) low-density polyethylene heavy-walled 30-liter bags. The bulk snow samples weighed up to 14 kg and consisted of one to several drill cores depending on the depth of the snow cover. The length and weight and the physical properties of each core were measured in the field. To avoid contamination during the field characterisation, a second bulk sample was taken at each sampling site for the major and trace elements analysis. To assess the microbial community composition, cores from the T03, G04 and M03 sampling sites (Fig. 1) were collected into large sterile *Whirl-Pak*® bags for DNA sequencing. Two additional snow cores at D05 and M03 locations (Fig. 1) were collected and divided into 21 and 44 cm increments, respectively. Old layers' or 'summer layers' representing snow older than the 2014-15 winter precipitation were collected into separate bags. After sampling, all snow samples were packed into insulated boxes to ensure no melting occurred during their transport to the storage facility or laboratory. Prior to analyses samples were kept in a mobile freezer at −24 °C.

### 4.2. Processing and snow sample analysis

Snow cores for chemical analyses were melted at 60 °C for 20−40 minutes depending on the snow volume. Meltwater was filtered through 0.2 µm Millipore cellulose acetate membranes using a peristaltic pump, pre-cleaned silicone tubing, and a 140 mm Sartorius® polytetrafluoropropylene filter holder. Acid washed high-density polypropylene bottles or vials, were used to collect samples for cation and trace metal analysis. Low- and high-density polyethylene bottles or vials, were used to collect samples for the other dissolved constituents measurements. Acid washed containers were used to collect samples for dissolved nutrient and dissolved organic carbon analysis (DOC). Amber glass bottles were used to collect filtered samples for pH measurements. Water samples collected for major and trace metal analysis were acidified using Suprapur® 0.5 % (v/v) $HNO_3$. Samples collected for DOC were acidified with 1.2 M concentrated HCl 2% (v/v). Note that the snow sampling and analysis in this study does not allow the differentiation between the wet and dry soluble contributions to precipitation, and thus only the 'bulk' precipitation chemistry is obtained.

The pH of filtered samples was measured several hours after its melting at room temperature using an Oakton pH electrode. The dissolved inorganic carbon (DIC), F, Cl, $SO_4$, $NO_3$ were quantified using an ion chromatograph IC−2000 Dionex. Cations and trace metals, were measured using a Spectro Cirus Vision inductive coupled plasma, optical emission spectrometer (ICP−OES) at the University of Iceland. Most of the snow samples were also analysed by inductive coupled plasma sector field mass spectrometer ICP−SFMS at ALS Scandinavia, Luleå, Sweden. Dissolved organic carbon (DOC) was measured at the Umeå Marine Sciences Centre, Sweden by combustion and analysis as $CO_2$ using a Shimadzu DOC-VPCH analyser. Samples for dissolved $PO_4$, $NO_3$, $NO_2$, were kept frozen until their colorometrical determination using an Alpkem AutoAnalyser. Analytical measurements had inter-laboratory reproducibility within 5.0 %.

The samples collected for DNA analyses were processed for DNA sequencing using methods previously described by Lutz et al. (2014; 2015). Further details of the snow sampling, DNA and $\delta^{34}S$ analyses are presented in Chapter 4ES2 in the Electronic Supplement 2.

### 4.3. PHREEQC calculations

Aqueous speciation, charge imbalance, and mineral saturation states of melted snow collected during this study were calculated using the PHREEQC 2.17 geochemical code (Parkhurst and Apello, 1999) together with its *phreeqc.dat* database after its update with the aqueous complex formation and mineral solubility constants reported by Gysi and Stefánsson (2011). These caculations were performed using the measured samples compositions, pH, and water temperature at time of melting provided in Tables 2 to 7. The *in situ* pH and saturation states were calculated assuming the melting temperature of 0.1 ºC and the DIC concentration as measured by ion chromatography. The fluid representing snowmelt was not allowed to equilibrate with atmospheric $CO_2$. The pH of the pure water at the temperature of 0.1 and 25 ºC was calculated assuming $CO_2$ concentration of 395 ppmv (Tans and Keeling et al., 2016). The pH of pure water in equilibrium with this atmospheric $CO_2$ concentration is 5.54 and 5.61 respectively at 0.1 and 25 ºC.

## 5. RESULTS

The bulk samples collected in this study represent the weighted average chemical composition of the total snow layer accumulated at the sampling locations on Vatnajökull glacier and highlands NE of the glacier (Fig. 1) from  September 2014 until March 2015 (Table 2 and 3). The boundaries between the 2014–2015 accumulation and the previous years are rather obvious and include higher frequency of ice lenses of different sizes, different size of snow crystals and/or the presence of dust. Ice lenses are formed due to the partial melting of glacial snow in the summer and its subsequent refreezing in the autumn. Dust transported during the summer can be captured in the refreezing ice. Coarser snow crystals are present in the lower part of the layer between winter seasons (Gislason, 1990). The 2014-15 Bardarbunga eruption lasted 181 days, from August 31 to February 27. The first snow fell in the highlands NE of the glacier on September 6 (IMO, 2017; Pálsson et al., 2015), indicating that snow samples collected during this study represents, apart from the first week, the entire eruption period. The uppermost part of the snow cores correspond to snow that fell after the eruption ended.

The D05 and M03 incremented cores were analysed to determine the chemical evolution of the snow as a function of depth, which can be translated to the timing of snow accumulation (Tables 4–6). These samples are denoted D05_1 for the youngest and uppermost D05 increment (accumulated just before March, 23 when the sampling was performed) to D05_21 for oldest snow within the snow accumulation period at this sampling point. Beneath the D05_21 increment, the ice lenses formed due to spring/summer melt confirming the boundary of the 2014-2015 snow layer.

Physical aspects and chemical compositions of the bulk snow and snow increments are presented in the Electronic Supplement 1 and Figs. 2-6. Figures 3 and 4 show depth of snow increments from the top to the bottom of the core, their names, lengths, and representative chemical compositions (pH and $SO_4$) within the D05 and M03 cores. The thickness of the winter layer and therefore length of the bulk cores reflect trends in precipitation and altitude. The northern part of Vatnajökull is within a “rain shadow”, whereas its southern slopes are characterized with precipitation up to 7,000 mm water equivalent (Björnsson and Pálsson, 2008). The length of the bulk cores ranged from 75 cm (B09) to 634 cm (M03) with an average of 364 cm. The longest cores (D12, G01, G04, BOR, B15, and M03) were sampled from the interior of the glacier and were more than 500 cm long. The amount of the 2014-15 winter precipitation on the Vatnajökull glacier varied; at the Dyngjujökull glacier, the winter precipitation equalled to 2.22 m water equivalents whereas within Grimsvötn-Gjálp area it equalled to 3.18 m water equivalents (Pálsson et al., 2015). The SE and SW wind carries most of the precipitation and the Holuhraun eruption site sits in the rain shadow from the Vatnajökull glacier (IMO, 2017).

The chemical charge imbalance of the snow samples, calculated using the PHREEQC computer code was less than 5.2% (average 2.1%) for bulk samples, 9.8% (average 5.1%) for the D05 increments, and 13.4% (average 3.1%) for the M03 increments. The arithmetic average of the chemical concentrations of the D05 and M03 increments are presented below and in Table 1. The greatest charge imbalance was calculated for the 'summer/old layers' (see Table 7). Those layers represent snow older than the 2014–2015 winter precipitation. It was sampled from beneath the bulk cores and it was characterized by coarser snow grains and/or ice lenses. Charge imbalance calculated for summer layers was as high as 36.9% (average 13.6%). This large charge imbalance is due to the dilute concentration of these layers; some chemical analyses were close to or below the detection limit. Lower concentrations in the summer layers stems from solute release during the partial melting of snow and lower sea spray effect due to lower wind speed in the summer time (Eiríksdóttir, 2008; Gislason, 1990; 1993).

The measured DIC might stem partly from the atmospheric $CO_2$ dissolving in the meltwater during sample processing. There is no correlation between average density and lengths of the cores. There is positive correlation between the depth of the increments and their average density in core D05 ($R^2$=0.36). There is strong dependence of the density and depth of the increments for the M03 core with $R^2$=0.54.

## 5.1. The pH of the 2014-15 snow accumulated close to the eruption site

The average measured pH at ambient temperature of the bulk samples, and the D05, and M03 increments were 5.08, 4.67, and 5.13, respectively. The measured pH distribution is shown in Fig. 2a. The isomaps presented in Fig. 2 are extracted from matrix surfaces (grids with 1000 m x 1000 m meshes) and calculated from measured values using kriging interpolation with linear variogram using Golden Software, Surfer13 software. The difference between measured and *in situ* (the pH of the meltwater at 0.1 °C) pH was 0.1. The average pH of the D05 and M03 increments was close to that of the bulk snow samples D05 and M03; with a 0.4 and 0.04 pH unit difference, respectively (Table 2, 4, and 6). At the Vatnajökull glacier, the lowest pH of 4.41 at 19.6 ºC was measured in D02 meltwater which core is located closest to the eruption site (Fig. 1 and 2) whereas the highest pH of 5.64 at 19.3 ºC was measured in meltwater from B09 (774 m a.s.l.).

The pH of all the bulk samples other than T03, B09, Sauða 01, Kiðufell 01, Kiðufell 02, Þránd, and Oddskarð was below the pH range of the reference snow (5.25-6.73; Gislason et al., 2000). Note that the reference snow from Langjökull was affected by the 2000 Hekla and perhaps the 1998 and 2004 Grímsvötn eruptions (Flaathen and Gislason, 2008; Gislason et al., 2000).

Generally, the pH of the 2014-15 snow decreases with depth as exemplified in the D05 and M03 snow cores. All but three of the D05 increments were more acidic than the reference snow (Fig. 3). The lowest pH was measured in increment D05_17 (pH 4.05 at 17.8 °C). Similarly, most of the

M03 increments pH values decrease with depth down to 300 cm (Fig. 4), but the correlation was not as strong as in the D05 increments. Below 300 cm, the pH in the M03 core increased slightly followed by drop down to 4.52 at 550 cm depth. The majority of the increments were more acidic than the reference snow.

## 5.2. Major and trace elements

### *5.2.1. Bulk snow samples*

The highest conductivity in the bulk samples was measured in the Hornbrynja core, 19.8 µS/cm and the lowest in B09, 3.6 µS/cm (Fig.1 and Table 2). For comparison the average conductivity in one of the direct runoff rivers Fjarðará, which has catchment extending up to the Fjarðaheiði mountain pass (Fig. 1) in East Iceland, is 33 µS/cm (e.g. Eiriksdottir et al., 2013). The highest concentrations of volcanic components such as $SO_4$, F and $H^+$ were measured in cores D01, D02, D05, Hornbrynja, and Sauða 02 (Table 3) exceeding those concentrations in the reference snow. The Cl, Na, Mg, K, $NO_3$, $NH_4$, B, Sr, and Li concentrations measured in bulk samples were within the range measured earlier in the reference snow. Concentrations of the metals Al, Fe, Mn, Ti, Ba, Cd, Co, Zn, Mo, Ti and V exceeded those measured in the reference snow in cores D01, D02, B13, Sauða 02, and Hornbrynja. Other constituents including REE were slightly higher than those previously measured in the reference snow with the highest in the Dyngjujökull cores. In general, concentrations of dissolved sea-spray cations such as Na, K, Mg, and Sr increase with increasing altitude in samples collected from the Vatnajökull glacier during this study, whereas this trend is not observed in the samples collected from the highlands northeast of the glacier. It is commonly observed that the sea spray effect on rain and snow composition decreases with distance from the sea and increasing altitude, however local topography can influence this effect (Gislason, 1990, 1993, 1996; Sigurdsson and Einarsson, 1988). A single storm can bring in high concentration of sea components inland and to high altitudes (Gislason, 1992).

Other components such as $NO_3$, $NH_4$, B, Br, and I also increased with increasing altitude, whereas Ca, P, Mn, V, Li, Ba, Cd, Co, Cr, Cu, Zn, Hg, Mo, Ti, Au, Hf, Nb decreased with increasing altitude. The pH, Cl, F, and $SO_4$ did not show this trend. Snow cores from the lowest altitude in the highlands NE of Vatnajökull glacier were wet, indicating partial melting of the snow (Kiðufell 01 and 02, Oddskarð).

All but three summer layers (D01_SL_ice lens, D12_SL, and Hornbrynja_SL) had at least one constituent that was more concentrated compared to its corresponding bulk core (Table 7). The $SO_4$/Cl ratios and Al and F concentrations in the summer layers compared to bulk cores can be seen in Figs. 2ES2 and 3ES2, in Electronic Supplement 2. The summer layers D01_SL, D07_SL, G04_SL, M02_SL had only one chemical constituent more concentrated than in the corresponding bulk core. In contrast, the summer layers B09_SL_2, BUDS_SL, Sauða 01_SL_ice lens, Kiðufell 01 soil had at least 10 chemical constituents, including K, P, and $NO_3$, more concentrated than in the corresponding bulk core.

### *5.2.2. D05 and M03 increments cores*

The variation with depth of pH and chemical compositions for core D05 are shown in Figs. 3 and 5 and Tables 4 and 5 and for core M03 in Figs. 4 and 6 and Table 6. These cores span from the beginning of the eruption to within 4 weeks after the end of the eruption. Generally, concentrations of most of the constituents including trace metals and REE ($SO_4$, F, Ca, Al, Fe, Mn, Ti, $NO_3$, Mn, As, V, Li, Cd, Co, Cu, Cr, Pb, Ni, Zn, Se, Be, Ag, Bi, Ga, Ge, Ir, Nb, Os, Pd, Re, Sc, Sn, Te, Tl, U, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu) increase with depth in the D05 core. Concentrations of most of the constituents exceeded concentrations measured in the reference snow in the lower part of this core (below 200 cm depth). In addition, there is more variation with depth in the chemical concentrations in the lower compared to the upper part of the core. Together with the lowest measured pH, the highest concentration of several constituents was in increment D05_17. In the M03 increments, seaspray constituents such as Na, Cl, K, Mg, Sr are most concentrated down to 100 m in depth. The lower parts of the cores are generally depleted in these seaspray ions. The Na, Cl, Mg, K, and Sr show very similar patterns with the depth.

## 5.3. Saturation states of the snow meltwater samples

Meltwater samples are undersaturated with respect to all common primary and secondary minerals, hydrated basaltic glass and amorphous secondary minerals phases found in the weathering environment of basalt (Gysi and Stefánsson, 2011) at 0.1 °C. The $pCO_2$ of the melted snow samples was lower than atmospheric $pCO_2$.

## 5.4. Microbial community composition and cell numbers

The results of the DNA sequencing of the T03 snow core are presented in Table 8. A total of 258 096 sequences passed the Qiime quality pipeline, corresponding to 591 operational taxonomic units clustered at 97% sequence identity. *Proteobacteria* was the most abundant phylum (94%) with *Gammaproteobacteria* (92%) being the overall dominant class and *Pseudomonas* (90%) the overall dominant genus. *Cyanobacteria* was the second most abundant phylum (4%) mainly being represented by the class *Synechococcophycideae* (3%) and therein the genus *Leptolyngbya* (2%).

The flow cytometry data for sample M03 and G04 showed 22735 and 24824 events respectively. For M03 this corresponds to $3.4 \times 10^5$ cell $mL^{-1}$ and 61.6% of the total events recorded, while for sample G04 this corresponds to $3.7 \times 10^5$ cells $mL^{-1}$ and 30.4 % of the total events recorded.

## 5.5. Sulphur isotopes

The sulphur isotope ratios for the snow and ice-core samples are listed in Table 3. The $\delta^{34}S_{SO_4}$ ratios were +5.8 to +16.6 ‰. These values range from those typically found for $SO_4$ in waters draining basaltic terrains towards that of seawater (Torssander, 1986; Gislason and Torssander, 2006; Gunnarsson-Robin et al., 2017; Rees et al., 1978).

## 6. DISCUSSION

### 6.1. Controls on rain water and snow chemical composition in Iceland

The chemical compositions of Icelandic precipitation has been monitored by the Icelandic Meteorological Office since 1958 (Eiríksdóttir, 2008; Gislason, 1990; IMO, 2017). Seaspray is the most abundant source of aerosols on land close to the oceans, whereas continental and manmade aerosols often dominate inland (Junge and Werby, 1958). Iceland is one of the most active dust sources on Earth with dust flux of 30-40 Mt/yr mainly coming from the glacier outwash planes, where the main component of the dust is basaltic glass (Arnalds et al, 2014). Dissolution of dust in rain water will increase pH and the concentrations of soluble rock forming constituents such as $SiO_2$, Ca, Mg, Na, and K depending on the dust chemical composition (Gislason and Eugster, 1987 a,b; Stefánsson et al., 2017a). Dust deposited with snow during winter will dissolve in meltwater during the spring, influencing the water chemical composition. Similar interaction of volcanic gases and tephra (volcanic ash, mostly glass) with atmospheric precipitation changes rain, snow and meltwater compositions (e.g. Flaathen and Gislason 2007; Olsson et al. 2013). Volcanic $SO_2$ hydrates and oxidizes in the atmosphere resulting in the formation of sulphuric acid $H_2SO_4$ (liquid aerosols; Lelieveld, 1993; Seinfeld and Pandis, 1988; Stefánsson et al., 2017a). Volcanic gases and aerosols can be transported over long distances, affecting rain composition away from their sources as has been observed during previous eruptions in Iceland (Flaathen and Gislason, 2007; Gislason et al., 2015; Thordarson and Self, 2003). For example, the 2010 Eyjafjallajökull eruption resulted in increased F concentration in rain water 100 km from the eruption vent (Eiriksdottir et al., 2014a).

### 6.2. Spatial and temporal evolution of chemical composition of the snow cover

In general, snow collected from the Vatnajökull glacier and the highlands northeast of the glacier was more acidic and polluted than the reference snow (Table 1). During the 2014-15 Bárðarbunga eruption, volcanic gases and aerosols caused the pH of snow in the vicinity of the eruption vents to be as low as 3.3 (Gislason et al., 2015; Galeczka et al., 2016). The eruption also affected the chemical composition of the snow, as shown by much higher concentrations of halogens and metals than recorded in the reference snow (Gislason et al., 2015; Galeczka et al., 2016).

The Na/Cl and Mg/Cl ratio of Icelandic precipitation in the absence of volcanism has been shown to be close to that of seawater (Gislason et al. 1996). The ratio of major ions in the snow relative to chlorine compared to that of seawater confirms volcanic and perhaps anthropogenic effects on the snow chemistry (Fig. 7). Most of the D05 core increments and bulk samples exhibited an excess of Cl compared to seawater (Fig.7). Because of this Cl excess, the elemental ratios of seawater (element/Na; Bruland, 1983) and the measured Na concentration in snow were used in this study to correct for the seawater aerosol contribution in measured snow compositions. The pH was higher and the concentrations of Na, Mg, Cl were lower in 1988 Vatnajökull snow collected by Gislason (1990) compared to present study, even in samples collected at similar locations (samples T03, T05, T08). Note that the 1988 samples were collected in June, meaning that part of this snow deposited during the early spring months of April, May, and part of June, when the wind speed is on average lower than during the high-winter (e.g. Gislason et al. 1990, 2015). The highest Cl concentration in the present study was measured in T05 and Hornbrynja (Fig. 1). This is consistent with a prevailing SE and SW winds which bring marine aerosols from the south to the Tungnaárjökull glacier.

The dissolved $SO_4$ concentrations were elevated in the BOR, Tungnaárjökull and Dyngjujökull cores and higher than in the Vatnajökull snow samples from 1988. Note however, that partial melting could explain some of the difference since the 1988 snow was collected in June and therefore spring melting could have flushed out some of the ions trapped in the snow (Gislason 1990; see chapter 6.5).

The most acidic snow samples were collected at Dyngjujökull with the lowest pH in cores D01 and D02. Those cores are the closest to the eruption site indicating that volcanic activity affected most the areas located the closest to the eruption vent. The proximity of the volcanic plume source and its effect on snow chemical composition might have been intensified by the topography in the area. The base of the orographic clouds contains the majority of the pollutants compared to the upper part of the cloud and therefore the most polluted snow precipitated on lower slopes of the Dyngjujökull glacier (Dore et al., 1992, 1996; Nawrot et al., 2016). Predictions of the atmospheric $SO_2$ distribution around Iceland during the eruption period based on the CALPUFF air quality model (Gislason et al., 2015) show, that atmospheric $SO_2$ concentration was higher than 350 $\mu g/m^3$ for 9-18 of the eruption days and the highest concentrations were close to the eruption site. This is in contrast to what was seen in the rain water affected by the 2014-15 Bárðarbunga eruption, where the lowest measured pH was observed relatively far from the pollution source (about 100 km NE of the eruption site; Gislason et al., 2015; Stefánsson et al., 2017a). This observation was explained by the time and therefore distance needed for $SO_2$ to oxidize and produce $H_2SO_4$ (Gislason et al., 2015, Stefánsson et al., 2017a). Dry air oxidation rate of $SO_2$ is a function of UV radiation and since the Bárðarbunga eruption occurred during the northern hemisphere winter, the UV radiation was low and the oxidation rate relatively slow (e.g. Flaathen and Gislason, 2007; Gislason et al., 2015). Oxidation in the close vicinity of the eruption vents is likely accelerated due to high temperature within the volcanic plume (Martin et al., 2006).

The strong correlation between uncorrected (Fig. 8) and seawater corrected (Fig. 9) $SO_4$, F, and Cl concentrations and *in situ* pH confirms that aerosols originating from the volcanic $SO_2$, HCl, and HF acidified the snow. Note that in general there was insignificant amount of particulates in the snow samples, therefore, the dissolution of basaltic sediments containing low Cl, F, and S concentrations (e.g. Óskarsson, 1981) would not account for high concentrations of these constituents in snow samples. The stronger correlation for Cl than for $SO_4$ concentrations versus *in situ* pH underscores the importance of HCl compared to $H_2SO_4$. This importance is likely due to higher Cl solubility and more rapid chemical pathways for HCl dissolution compared to $SO_2$. This suggests that there is limited oxidation of $SO_2$ apart from its initial high temperature oxidation since the eruption released 100 times more $SO_2$ than HCl (Gislason et al. 2015). If all the seawater uncorrected $SO_4$, Cl, and F was assumed to be derived from HCl, HF and $H_2SO_4$, the pH of the samples would be lower than that measured, as shown in Figure 10a. The calculated pH, based on seawater corrected $SO_4$, Cl, and F concentrations are close to the in situ pH up to pH ~5 (Fig. 10b). At neutral pH, the calculated pH is higher than measured pH for the M03 core increments. This might stem from an overcorrection of the seaspray component for Cl, $SO_4$ and F, or by the addition of volcanogenic Na in snow samples.

Hydrogen halides (Br, F, Cl, I) are highly soluble meaning that they are easily scavenged by rain or snow within hours to a few days, thus their effect on troposphere is local (Grellier et al., 2014). The seaspray constituents in the uppermost part of the M03 core are highly influenced by the changes of the wind direction and speed during the spring season and therefore the concentrations show considerable variation (Fig. 6).

Clearer correlations between pH and halogens are observed for the D05 than the M03 increments (Fig. 8 and 9). This is mainly due to the proximity of this sampling location to the eruption vent. Although the Maríutungur cores are further from the eruption site than the Dyngjujökull cores, they have also been affected by the volcanic activity as indicated by their increased $SO_4$ concentration compared to Cl. The Cl concentration in the Maríutungur cores is comparable to that of the Dyngjujökull cores, which have been the most affected by the volcanic eruption. Because the $SO_4$ and F concentrations in seawater are lower than Cl, the absolute concentrations of $SO_4$ and F in snow influenced by volcanic plume are much more evident than for Cl. The decrease in pH and increase in volcanic aerosols with depth reflects changes in effusion and emission rates throughout the volcanic eruption. The highest concentration of $SO_4$ was observed in the increment with the lowest pH (D05_17). This snow precipitated during the first months of the eruption. In September and October, the effusion and emission rates were the highest (Gislason et al., 2015). Similarly, during the Laki eruption, most of the volatile mass (~60%) was released during the first 1.5 months of the eruption (Thordarson et al., 1996).

The highest pH was measured in bulk core B09, which was relatively close to the eruption site. However, this sample had lower $SO_4$, Cl and F concentrations than samples collected at Dyngjujökull (Table 3), and it also had greater amounts of embedded sediments (basaltic dust transported mostly from highlands). The dissolution of basalt increases meltwater pH (e.g. Gislason and Eugster 1987a; Galeczka et al 2014b). Similarly, a slightly higher pH compared to the glacier snow was observed in samples collected from the highlands northeast of the glacier. The lowest conductivity was found in core B09. Its conductivity of 3.6 µS/cm might be due to previous partial melting of this core at its relative low altitude (774 m.a.s.l.) and geographical setting – the sample spot might have been protected by the Kverkfjöll mountain range (Fig. 1).

As can be seen in Fig. 11, protons ($H^+$) balanced about half of the negatively charged anions in the bulk D05 core, ~10% in the bulk M03 core and ~70% in the most polluted sample, the D05_17 increment. Also this increment had the highest contribution of $SO_4$ into charge balance. The dominating anion in all snow samples was Cl, which mostly originates from seaspray. The seaspray contribution was the highest in samples least affected by the volcanic eruption (e.g. M03 as seen on Fig. 7) confirming seaspray as main source of the dissolved ions in these samples. The contribution of non-marine cations, such as Al and Fe, increases in samples which were the most affected by the volcanic gases and/or aerosols.

The concentrations of Al, Fe, Mn, V, As, Ba, Cd, Co, Cr, Cu, Pb, Se, Ti, Ag, Pd, Re, Te, Tl, Y, and all REE were highest in the cores from Dyngjujökull (Fig. 1); most often the highest values were found in cores D01 or D02 (Table 3). The Al, Fe, Cu, Pb, Se, Ti, Ag, Pd, Re, Te, Tl, Y, and all REE show positive correlations with the sum of $SO_4$, Cl, and F with ($R^2>0.5$) suggesting that these elements were degassed at depth and transported in the gas phase of the eruption as chlorides, fluorides and/or sulphate aerosols/salts (e.g. Moune et al., 2006; Gauthier et al., 2016). Most metal concentrations also increased with decreasing pH, confirming their addition due to volcanic acidic gases. The positive correlation between metals e.g. Al which is refractory with volcanogenic ions suggests transport of these metals within the plume; in this case Al as fluoride and chloride species (Calabrese et al., 2011). In addition, the concentration of particulates was low in the snow samples; no correlation between pH, metal concentration or particulate concentration was found, confirming insignificant effect of basaltic particle dissolution into the ion budget. Note, that although the snow cores were melted at around 60 °C the meltwater temperature was close to 0 °C right after melting, and the contact time between particles and meltwater before its filtration was short (less than an hour). Dissolution rates of basaltic glasses decrease with decreasing temperature (Gislason and Oelkers, 2003). The $SiO_2$ concentration was very low in all the melted snow samples, confirming the insignificant contribution of basaltic particle dissolution on the chemical composition of the snowmelt.

The compositions of all elements in all snow samples, apart from some of the incremental samples, were within European drinking water standards (European Community, 1998). The D05 increments from near the bottom of the core exceeded the limits for Al given by World Health Organization (WHO, 2006). Snow collected in vicinity of the eruption site during the 2014-15 Bárðarbunga eruption was acidic, with pH ranging from 3.34 to 4.85, and with F, Al, Fe, Mn, Cd, Cu, and Pb concentrations surpassing drinking water standards (Galeczka et al. 2016; Gislason et al., 2015; European Community, 1998).

The major hazard related to snow acidification is proton and metal mobility. Metal mobility increases with decreasing pH and acidic snowmelt will increase dissolution of particles embedded in the snow/ice and the bedrock, potentially provoking further toxic metal release. Kepski et al. (2016) reported that more than half of pollutants in snow were released with the first 14% of the snow melt. Partial melting of snow can result in factor of five concentration increase in the initial meltwaters (Johnnessen and Henriksen, 1978; Gislason, 1990). Taking as an example the bulk sample D02 and its *in situ* pH of 4.41 (Table 2), the partial melting would decrease the meltwater pH to about 3.7 (calculated by multiplying the proton activity by factor of 5). Similarly, the initial melt from the all the bulk samples with an average *in situ* pH of 5.09 could be as low as 4.4. This decrease of pH would increase the solubility of the solid $Al(OH)_3$ by a factor of 3.

It should be pointed out however that some of the negative environmental impacts of snow acidification are attenuated by water-rock interaction. The increased host rock dissolution caused by acidic snowmelt can mobilize the elements limiting biological activity such as Fe (White, 1999). Moreover, toxic metal scavenging (oxy)hydroxides will precipitate from the meltwaters as mineral-fluid reactions neutralize the acidic waters (Aiuppa et al., 2000a,b, Flaathen and Gislason, 2007, Flaathen et al., 2009). Note also that the fluoride sourced from volcanic HF and F aerosols/salts will increase basalt dissolution rates (Wolff-Boenisch et al., 2004) further accelerating the neutralization of the acidic snowmelt.

### 6.3. Temperature, partial melting, and constituent fractionation with depth

The concentrations of most ions increase with depth in core D05; this increase is more pronounced after correcting these concentrations for seawater input. It seems likely that this increase is related to the intensity of the volcanic emissions and effusion rates. This trend is not seen for ions of marine origin, such as Na (Fig. 5). Air temperature measurements carried out by the IMO on the Brúarjökull glacier (see the weather station location in Fig. 1) indicate that the first drop of temperature below 0 °C was at the end of September 2014 and the temperature remained below 0 °C, with the coldest period from February until April (Fig. 4ES2 in Electronic Supplement 2). From the end of September until April, there were short periods when the temperature increased above 0 °C possibly leaving thin ice lenses in the snow. Higher concentrations of ions in the summer layers of the snow in the vicinity of Brúarjökull (B09, B15, BUDS; Table 7) confirms that it might have partially melted during the winter. Partial melting tends to flush ions out from the snow into the meltwater. Most of the salts, aerosols, and pollutants are present on the surface of the snow crystal and thus readily removed by meltwater (Gislason, 1990; Johannessen and Henriksen, 1978). The concentration of several ions in the summer layers collected from the highlands were higher than the corresponding bulk snow samples, suggesting partial melting. In general, most of the summer layers are dilute comparing to bulk snow, however, the $SO_4$/Cl ratio in the summer layers is often higher than the bulk snow samples (Fig. 2ES2 in Electronic Supplement 2). Note, that due to physical and chemical properties (its larger hydrated radii), Cl is released faster than $SO_4$ (Gislason, 1990).

### 6.4. Volatile concentrations in the snow and in the volcanic plume

The molar ratios of volatile components in the snow samples were substantially different than that of the plume. The average bulk snow S/Cl ratio is closer to that of seawater than to that of the plume. The S/Cl and F/Cl molar ratios in the plume were 55 and 0.9, respectively (Gislason et al., 2015; Stefánsson et al. 2017a), whereas these ratios in seawater are 0.05 and $1.24 \times 10^{-4}$, respectively (Bruland, 1983). The average bulk snow molar ratios are equal to 0.09 for S/Cl and 0.01 for F/Cl. The highest ratios in the D05 increments were 0.7 and 0.2 for S/Cl and F/Cl, respectively. The seawater corrected ratios are an order of magnitude higher. Nevertheless, they are always lower than the gas plume ratios. Although the snow chemical ratios are lower than the plume ratios, comparison between the seawater derived and total S, Cl, and F concentrations in the bulk and D05 increments, after the sodium correction as described earlier, indicates that up to 96% of $SO_4$, up to 70% of the Cl, and up to 100% of the F, was sourced by the volcanic plume. In this estimation, due to small amount of basaltic dust in the snow samples, and the low concentration of these components in basaltic glass, rock derived S, Cl, and F were neglected. In addition, the volume of tephra produced during this eruption was not substantial (Gudmundsdottir et al., 2016). All collected snow samples had >90% of F derived from volcanic plume. Majority of the samples (54 %) had more than half of the total S sourced from volcanic aerosols. Calabrese et al. (2011) observed that the rainwater in vicinity of Etna volcano reflected the composition of the volcanic plume and concluded that element fractionation occurs during the scavenging of plume-derived elements. The relative concentrations of these volatiles in the plume compared to the snow demonstrates that Cl and F are much more efficiently taken up by snow surfaces than S.

Further insight into the origin of volatile elements in the Vatnajökull snow was gained from sulphur isotope $\delta^{34}S$ fractionation, mixing models and reaction path simulations (Fig. 12). The principles behind the geochemical calculations applied here have been described elsewhere, i.e. non-reactive mixing and reaction path calculations (e.g., Zhu and Anderson, 2002). In order to trace the origin of the dissolved volatiles including sulfur, a non-reactive mixing between two fluids was calculated, based on the end-member fluid chemical and isotope composition and the corresponding mixing ratios. No chemical reactions were allowed during the mixing calculations. The mixing model applied in this study has previously been described by Stefánsson et al. (2017a). In addition, reaction path modelling was used to evaluate the changes in pH of the rain water due to volcanic gas addition and interaction with rock aerosols. The initial water used in the model was rain water with the chemical composition reported by Stefánsson et al. (2017a). The rock aerosols was assumed to be that of typical Icelandic basalts as reported by Galeczka et al. (2014b) for major elements and S and Cl concentrations was taken from Kaasalainen and Stefánsson (2012). The composition of the volcanic plume was taken from Burton et al., 2015, Sigvaldason and Elíasson (1968) and Stefánsson et al. (2017a). For the calculations the $\delta^{34}S$ of rock aerosols and $SO_2$ was taken to be that of average basalts (Stefánsson et al., 2017b). Moreover, it was assumed that $SO_2$ had been fully oxidized in the rainwater to form $H_2SO_4$. In the first simulation, rain water was reacted incrementally with basalt in a closed system, and no secondary minerals were allowed to precipitate. In the second simulation, rain water was reacted incrementally with S (taken to be $H_2SO_4$) and Cl (taken to be HCl) in proportions measured in the volcanic plume (Stefánsson et al., 2017a). Results of the mixing calculations and reaction path modelling (rain water─basalt and rain water-volcanic gas interaction) were compared with the measured snow chemical composition to distinguish between basaltic rock aerosols and volcanic gas input (e.g., Gunnarsson-Robin et al., 2017). The $^{34}S$ isotope composition of the snow collected during this study indicates that the seawater $^{34}S$ signal ($\delta^{34}S$ of 21 ‰; e.g. Marini et al., 2011) decreased with the distance from the shore. Snow collected closest to the eruption site was the most depleted in $\delta^{34}S$ compared to seawater. This is consistent with the greater seawater Cl and Na concentrations in the snow closer to the shoreline. The calculated $\delta^{34}S$ fractionation obtained from the non-reactive mixing of unpolluted rainwater of marine origin with basalt and volcanic gas, respectively, results in similar trends – the depletion of $\delta^{34}S$ (Fig. 12a). In general, the $\delta^{34}S$ composition of samples collected during this study, and in vicinity of the Holuhraun lava (Galeczka et al., 2016), compares better when the volcanic gas rather than basalt is mixed with the rain water. The pH versus $\delta^{34}S$ of the rain water and basalt and rain water and volcanic gas interaction show distinct trends (Fig. 12b). With the decreasing $\delta^{34}S$, the pH of the modelled fluid increases from the initial pH of 5.7 when basalt is disolved in the rain water whereas the pH decreases when volcanic gas is dissolved. Comparison of those trends with the chemical composition of the snow connfirms the presence of volcanically derived S in the snowmelt.

### 6.5. Enrichment ratios of the volatiles and trace metals in the Vatnajökull snow

The enrichment factor (EF) indicates the enrichment or depletion of a given element in snow relative to the volcanic plume. This was calculated by dividing snow concentration ratio of the element of interest normalized to a reference element, by the same concentration ratio in the volcanic plume. Following Gauthier et al. (2016), Mg was used as normalizing element in this study. Trace and volatile element concentrations in the plume were taken from Gauthier et al. (2016). As can be seen in Fig. 13, all “volatile” elements were depleted in the snow relative to the plume with the greatest depletion for S. Similar trends were found in the most acidic snow collected close to the Holuhraun lava (Galeczka et al., 2015). As such, S is least efficiently snow trapped volatile element in the near vicinity of the Bárðarbunga volcanic eruptions. The least depleted element in the snow relative to the plume was Se. Similar, Se was found as one of the most enriched elements in the plume relative to the Holuhraun lava (Gauthier et al., 2016). The Se is an essential element for the biota, however, it can be toxic if concentrations exceed acceptable limits. Volcanogenic Se is mobile due to its relatively low vaporization temperature. Oxidation and cooling processes in the atmosphere will transform Se to soluble selenite ($SeO_3^{2-}$) and selenate ($SeO_4^{2-}$; Wen and Carignan, 2007) resulting in its high concentrations in the plume and therefore in snowfall and rainfall (Floor et al., 2011). Low amounts of Se have been found in Icelandic hay and herbage (Eiríksdóttir et al. 1981, Símonarson et al. 1984) resulting in Se deficiency occurring ubiquitously in lambs (Jóhannesson et al., 2007). Melting of snow enriched in Se might increase Se fluxes into to the surface waters and therefore making it available for biota. The relative enrichment factor of major cations and anions in precipitation relative to Cl and seawater was calculated by Stefánsson et al. (2017a). They shows that the $SO_4$ and F were greatly enriched in the precipitation compared to seawater suggesting that these volatiles were sourced from gas emission in addition to seawater spray.

## 6.6. The influx of chemical components on Vatnajökull glacier

The deposition fluxes of specific elements on the surface of Vatnajökull glacier were calculated using chemical concentrations of the snow cores collected on the glacier, their weights and dimensions, and the time of the snow accumulation; in this case the time from the first snowfall to the snow sampling was assumed to be six months. The term ‘flux’ represents the mass of the specific constituents deposited with the snow onto the glacial surface over a specific period of time, in mg/m$^2$/month. The volatile fluxes distribution over the studied area are shown in Fig. 2 b,c,d. The average fluxes of volatiles corrected for seaspray addition were 25.5 for S; 75.2 for Cl, and 3.7 for F; all in mg/m$^2$/month. The average seawater uncorrected S and Cl fluxes were within the range measured earlier at the Mjóanes rain monitoring station in SW-Iceland (Eiriksdottir et al., 2014a; Eiriksdottir and Sigurdsson, 2014b). In contrast, the F flux on Vatnajökull glacier was almost 4 times greater than at the Mjóanes station. Note, that Mjóanes location (Fig. 1) is distinct from that of the Vatnajökull glacier and therefore the effect of seaspray, dust and other local variabilities on precipitation differs. In addition, Mjóanes precipitation is affected by geothermal activity (Eiriksdottir et al., 2014a; Eiriksdottir and Sigurdsson, 2014b). Despite these differences, due to lack of more recent data, the Mjóanes element fluxes were used for this comparison. The S fluxes exceeded those calculated for Mjóanes in the cores collected closest to the eruption site (all Dyngjujökull cores), whereas F fluxes were higher in all but the M01 core. The highest S and F fluxes were calculated for core D01 (Fig. 2 b,c,d). This confirms the effect of the proximity of the eruption site on the monthly fluxes of volcanogenic volatiles. Due to lack of data on the intensity of snowfall with time, the deposition rates of the elements were not calculated. The volatile concentrations in the Vatnajökull snow were within the range of those measured in rain collected at IMO monitoring stations from September 2014 until February 2015 (Stefánsson et al., 2017a). However, the maximum rain concentrations are considerably higher than the highest concentrations measured in the snow samples collected in this study. Note, that the most acidic rain water was found at more distal locations than the snow samples collected during this study, suggesting low temperature oxidation of $SO_2$.

## 6.7. Microbial community composition

Sufficient DNA for sequencing identification was only obtained from core T03, and average cell numbers were determined in snow from samples G04 and M03. The average cell numbers evaluated by flow cytometry (~ $10^5$ mL$^{-1}$) were in the range of previously reported values for spring and summer snow (Amato et al., 2007; $10^3$-$10^5$ cells mL$^{-1}$). The sequencing showed that in core T03, the most abundant genus was *Pseudomonas*, which belongs to the *Proteobacteria* phylum within the *Bacteria* domain. The *Pseudomonas* species are known as plant pathogens and for their ice-nucleating capacities (Morris et al., 2010). While *Pseudomonas* taxa are widespread in many environments, they were also described as present, yet not dominant in Greenland and Svalbard spring snow after fresh deposition (Larose et al., 2010; Cameron et al., 2015). In Iceland, samples of summer snow collected during June to August of 2012 to 2014 (Lutz et al., 2015), revealed also a dominance of *Proteobacteria* (however mostly *Betaproteobacteria* and not *Pseudomonas*) early in the melting season, and *Bacteroidetes* later in the melting season. Although, both in core T03 and the summer snow described in Lutz et al. (2015) the bacterial community was dominated by the *Proteobacteria* phylum, it is important to note that at the genus level the differences are substantial. The main reason for this is likely because the microbial biomass in summer snow across the Artic is dominated by cosmopolitan snow algae, while the bacteria are a smaller part of the biomass (Lutz et al., 2016, 2017). We found that *Pseudomonas* dominated in core sample T03. Among the genus *Pseudomonas,* the species Pseudomonas *syringae* is known to be an ice nucleating bacteria and thus it is possible that by inducing the freezing of atmospheric water droplets, these ultralight bacteria, actively enhance snow deposition (Morris et al., 2008), explaining their high abundance in the freshly deposited snow. As *Pseudomonas* is widespread in freshly deposited snow (Larose et al., 2010; Cameron et al., 2015), it appears that the high amounts of aerosols created by the 2014-15 Bárðarbunga eruption did not substantially affect the microbial community composition in our snow samples.

### 6.8. Scavenging potential

The average depositional flux calculated for sampling sites (see Chapter 6.6) located within the specific Vatnajökull glacier outlets and their respective areas (Fig. 1; Pálsson et al., 2015) were used to estimate the total S, Cl, and F deposition flux during the winter. The comparison between these fluxes and the total mass of S, Cl, and F released during the eruption period was used for estimating the snow scavenging potential of the volatiles. The total mass of S deposited within the accumulated winter snow was: 293 tonnes at Dyngjujökull glacier, 163 t at Brúarjökull, 25 t at Tungnaárjökull, 24 t in Grímsvötn area, and 9 t at Maríutungur. The total mass of Cl was 1130 t at Dyngjujökull glacier, 375 t for Brúarjökull, 54 t at Tungnaárjökull, 64 t in Grímsvötn area, and 16 t at Maríutungur. Finally, the total mass of F was 42 t at Dyngjujökull glacier, 16 t at Brúarjökull, 5 t at Tungnaárjökull, 4 t in Grimsvötn area, and 1 t for Maríutungur. Although the greatest mass of deposited volatiles was found in the snow accumulated at Dyngjujökull, it scavenged only 0.005%, 1.16%, and 0.09% of total S, Cl, and F released during eruption period, respectively. This observation confirms that the deposition and scavenging potential close to the eruption site (up to several tens of km) was minor compared to the mass of emitted gas. It also suggests that residence time of gases/aerosols in the atmosphere is long. Similarly, Calabrese et al. (2011) found that more than 90% of volcanogenic trace elements were dispersed to at least 10 km from the volcanic source and only 0.05-0.5% of S, 0.1-1.1% of Cl, and 0.05-0.3% of F released to the atmosphere was deposited within 10 km distance from the summit. Moreover, the higher scavenging of Cl compared to S in our studies samples is consistent with the conclusion that substantial distance is needed for $SO_2$ to oxidize and produce sulphuric aerosols which is favourable to uptake by snow (Gislason et al., 2015, Stefánsson et al., 2017a). Taken together, these observations also suggest that although snow cores preserve volcanic signals and therefore can be useful to identify past volcanic events, due to the minor scavenging potential of this snow and partial melting, detailed chemical composition of past volcanic plume cannot be obtained from the analysis of historic snowfalls.

## 7. CONCLUSIONS

There are several major conclusions that can be drawn from this study on the chemical composition of the snow deposited during the 2014-15 Bárðarbunga eruption:

1. Despite the fact that 2014–15 Bárðarbunga eruption was the largest eruption around the North-Atlantic in more than 200 years, the toxic and heavy metals concentrations of its surrounding snowpack did not exceed drinking water standards given by European Commission (EC, 1998).

2. Environmental impact of the volcanic eruptions varies with time. The highest gas emission and lava effusion rates were measured during first weeks of the eruption (Gislason et al., 2015). This was reflected by the highest acidity and metal concentration of the deepest and oldest part of the snow cores.

3. The highest concentrations of volatiles in the snow cores were found close to the eruption site on the Dyngjujökull glacier. This confirms the results of the $SO_2$ gas dispersion CALPUFF air quality model (Gislason et al., 2015) which predicted that the same area would be one of the most affected by the volcanic plume.

4. Proximity of the rich in $SO_4$ snow cores to the eruption site confirms that the $SO_4$ was probably sourced from the high temperature $SO_2$ oxidation within the volcanic plume. Otherwise, the highest $SO_4$ concentrations would have been expected in the snow cores further away from the eruption site, similar to what was found in the rain water samples (Stefánsson et al., 2017a).

5. The snow scavenging potential close to the eruption site (up to several tens of km) was minor. The snow removed only up to 1.2% of Cl, less than 1% of F, and less than 1‰ of total S released during the entire eruption period. It confirms that the snow has limited cleaning capability of the volcanic pollutants from the air. It also confirms long life-time of volcanic volatiles in the atmosphere.

6. The microbial communities were similar to those found in other parts of the Arctic, confirming a minor impact of this eruption on the microbial ecology within the snow.

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## Figure captions

Figure 1. Sampling locations on the Vatnajökull glacier and in the highlands NE of the glacier. The grey area labelled Holuhraun lava, represents the extent of this lava after the 2014-15 Bárðarbunga eruption. The weather stations operated by IMO on Brúarjökull, Hágöngur, and Kárahnjukar are shown as diamonds. The cross represents the Maríutungur area. The Þránd is the snow sample located at the Þrándarjökull glacier. The two dots superimposed on the map of Iceland depict the IMO rain monitoring station at the Mjóanes, and the snow coring location on the Langjökull glacier, respectively. The G01, G04 and BOR sampling locations are within the Gjálp-Grimsvötn area (see text).

Figure 2. Spatial distribution of the measured pH (a) of the bulk snow cores on the Vatnajökull glacier and in the highlands NE of the glacier. The (b), (c), and (d) illustrate the seawater corrected flux of S, Cl , and F, respectively; in mg/m$^2$/month, see text.

Figure 3. The pH and dissolved $SO_4$ concentration (as measured with IC) of D05 snowmelt water as a function of increment depth. The vertical line on the pH plot represents the pH of the pure water equilibrated with 395 ppmv of $CO_2$ at 25 ºC as calculated with the PHREEQC computer code. The sampling site is located at an elevation of 1206 m.a.s.l.

Figure 4. The pH and dissolved $SO_4$ concentration (as measured with IC) of M03 snowmelt water as a function of depth. The vertical line on the pH plot represents the pH of the pure water equilibrated with 395 ppmv of $CO_2$ at 25 ºC as calculated with the PHREEQC computer code. The sampling site is located at an elevation of 1331 m.a.s.l.

Figure 5. The concentrations of major and trace dissolved elements with depth in snow core D05. Snow that fell during the most effusive period of the volcanic eruption in early winter is located in the deepest part of the snow core.

Figure 6. The concentration of major and trace dissolved elements with depth in snow core M03. Snow that fell during the most effusive period of the volcanic eruption in early winter is located in the deepest part of the snow core.

Figure 7. The ratios of elements to Cl in the snowmelt collected from the Vatnajökull glacier and the highlands NE of the glacier, and from the reference Langjökull winter snow collected in 1997–2006. The seawater ratio was taken from Bruland (1983).

Figure 8. The concentrations of selected elements as a function of the *in situ* pH (at 0.1 °C) of the snow samples. The *in situ* pH was calculated using PHREEQC computer code.

Figure 9. The concentrations of selected components in snow versus *in situ* pH. Concentrations were corrected for the seawater component as described in the text. The *in situ* pH was calculated using PHREEQC computer code.

Figure 10. The theoretical pH calculated based on the seawater uncorrected (a) and seawater corrected (b) Cl, $SO_4$, and F concentrations versus *in situ* pH of snow samples.

Figure 11. The aqueous species dominating the charge balance of the D05 bulk core (a, b), M03 bulk core (c, d), and in the most acidic increment D05_17 shown as percent of charge contributed by each species. Cations are illustrated on the left (a, c, e), anions on the right (b, d, f). Speciation distribution was calculated at 25 ºC using measured dissolved constituents and the PHREEQC computer code.

Figure 12. The results of the mixing model between rain water and volcanic gas and rain water and basalt (a) and the reaction path simulation (b). The lines represent the theoretical composition of the final fluid when basalt (simulation 1) and volcanic gas (simulation 2), respectively are assumed to be dissolved in unpolluted seawater originating rain water. The dots represent measured concentrations in the snow.

Figure 13. Enrichment factor in snow collected during this study with respect to Holuhraun gas plume (Gauthier et al., 2016) for several trace elements and volatiles relative to Mg. The symbols represent the average enrichment factor for bulk snow cores, the D05 and M03 increments, and the Holuhraun snow (Galeczka et al., 2016). The error bars represent the standard deviation.

## Table captions

Table 1. Comparison of the average, minimum, and maximum pH, conductivity (Cond.), and dissolved constituents concentrations between snow samples collected from the Langjökull glacier in 1997–2006 and from the Vatnajökull glacier in 2015. The Vatnajökull snow samples are presented both as bulk samples and as D05 snow core increments.

Table 2. The logistics and physical parameters of the bulk snow samples collected from the Vatnajökull glacier in 2015. The temperatures given in the table are reference temperatures at which pH and conductivity were measured. The *in situ* pH and charge imbalance were calculated using the PHREEQC computer code at *in situ* melting temperature of 0.1 ºC (Parkhurst and Appelo, 1999).

Table 3. Concentrations of dissolved constituents and S isotopes in melted bulk snow samples from Vatnajökull glacier and the highland NE of the glacier. Values in italics were measured by ALS Sweden (see text). The uncertainty for $\delta^{34}$S analyses is ±0.2 ‰.

Table 4. Measured pH and conductivity at the temperature given in the table (T [°C]/pH; T [°C]/Conductivity), and chemical composition of the increments from the D05 core. The charge imbalance and *in situ* pH was calculated using the PHREEQC computer code at *in situ* melting temperature of 0.1 ºC. Increment numbers increase with depth; D05_1 was located at the surface whereas D05_21 was at the bottom of the winter snow layer. Weight of sediments in all increments were <0.01 g.

Table 5. Concentration of dissolved constituents in melted snow samples collected from the D05 core increments. Values in italics were measured by ALS Sweden (see text).

Table 6. Measured pH, conductivity at the temperature given in the table (T [°C]/pH; T [°C]/Conductivity) and chemical composition of the M03 core increments. The charge imbalance and *in situ* pH was calculated using the PHREEQC computer code at *in situ* melting temperature of 0.1 ºC. Increments numbers increase with depth; M03 1 was collected at the surface, whereas M03 44 was at the bottom of winter snow layer.

Table 7. Summer layers collected below the respective bulk snow samples, their names, measured pH, conductivity at the temperature given in the table (T [°C]/pH; T [°C]/Conductivity) and chemical composition. The charge imbalance and *in situ* pH was calculated using the PHREEQC computer code at *in situ* melting temperature of 0.1 ºC.

Table. 8. Bacterial community composition in sample T03 based on 16S rRNA gene sequences and OTU clustering at 97% similarity. Table shows taxa with > 0.1% relative abundance.