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The chemical composition of rivers and snow affected by the 2014/2015 Bárðarbunga eruption, Iceland

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Abstract

The 2014/15 Bárðarbunga volcanic eruption was the largest in Iceland for more than 200 years. This eruption released into the atmosphere on average 60,000 tonnes/day of SO_2, 30,000 tonnes/day of CO_2, and 500 tonnes/day of HCl affecting the chemical composition of rain, snow, and surface water. The interaction of these volcanic gases with natural waters, decreases fluid pH and accelerates rock dissolution. This leads to the enhanced release of elements, including toxic metals such as aluminium, to these waters. River monitoring, including spot and continuous osmotic sampling, shows that although the water conductivity was relatively stable during the volcanic unrest, the dissolution of volcanic gases increased the SO_4, F, and Cl concentrations of local surface waters by up to two orders of magnitude decreasing the carbon alkalinity. In addition the concentration of SiO_2, Ca, Mg, Na and trace metals rose considerably due to the water−molten lava and hot solid lava interaction. The presence of pristine lava and acidic gases increased the average chemical denudation rate, calculated based on Na flux, within Jökulsá á Fjöllum catchment by a factor of two compared to the background flux.

Melted snow samples collected at the eruption site were characterized by a strong dependence of the pH on SO_4, F and Cl and metal concentrations, indicating that volcanic gases and aerosols acidified the snow. Protons balanced about half of the negatively charged anions; the rest was balanced by water−soluble salts and aerosols containing a variety of metals including Al, Fe, Na, Ca, and Mg. The concentrations of F, Al, Fe, Mn, Cd, Cu, and Pb in the snowmelt water surpassed drinking− and surface water standards. Snowmelt−river water mixing calculations indicate that low alkalinity surface waters, such as numerous salmon rivers in East Iceland, will be more affected by polluted snowmelt waters than high alkalinity spring and glacier fed rivers.

1. INTRODUCTION

Volcanic eruptions can influence global climate through degassing and aerosol formation (Mather et al., 2015; Oppenheimer, 2003; Robock, 2000, 2015; Thordarson and Self, 2003). Volatile components sourced from eruptive magmas affect major geochemical cycles (e.g. Delmelle et al., 2007, 2015; Frogner et al., 2001; Jones and Gislason, 2008; Williams−Jones, 2015). Young volcanic rocks experience rapid chemical weathering increasing the transport of dissolved constituents to the oceans (Jones et al., 2011; Eiriksdottir et al., 2013c; 2015). Weathering rates are further accelerated by the input of acids formed by the dissolution of volcanic gases such as SO_2, CO_2, HCl, and HF, and aerosols into atmospheric vapour, rain, and surface waters (e.g. Aiuppa, 2009; Aiuppa et al., 2006; 2007; Bagnato et al., 2013; Bobrowski et al., 2007; Calabrese et al., 2011; Cuoco et al., 2013; Delmelle, 2003; Delmelle et al., 2002; D'Alessandro et al., 2013; Floor et al., 2011; Frogner et al., 2001; Flaathen and Gislason, 2007; Flaathen et al., 2009; Gislason et al., 2002; Menard et al., 2014; Olsson et al., 2013). These acids will 1) lower the fluids' pH, 2) decrease the fluid's alkalinity, 3) increase the concentrations of anions derived from volcanic gas dissolution such as SO_4, F, Cl and 4) increase mineral dissolution rates and thus accelerate metal release to the fluid phase.

This study is focused on surface water−lava–volcanic gas interaction during the 2014/15 Bárðarbunga eruption in Iceland. This eruption provides a unique opportunity to study these interactions, as it was the largest eruption in Iceland since the 1783/84 Laki eruption (Gislason et al., 2015); this former eruption produced 15.1 km^3 of lava and released 122 Mt of SO_2 into the atmosphere, maintaining a sulfuric aerosol veil over the Northern Hemisphere for more than five months (Thordarson and Self, 2003). The amount of SO_2 released was comparable to the annual peak global man−made SO_2 emissions, which occurred during 1970−1980 (Smith et al., 2011). The Laki eruption killed 60% of the grazing livestock and 20% of the human population in Iceland (Thordarson and Self, 2003). Many of these deaths were likely caused by fluorine poisoning (Grattan and Charman, 1994; Steingrimsson and Kunz, 1998; Thorarinsson, 1969).

The timing of eruptions occurring at high latitudes can be crucial for their environmental impact. The 2014/15 Bárðarbunga eruption lasted throughout the winter, and therefore it affected the snow accumulated in vicinity of the eruption. Trace elements and major water–soluble ions emitted into the atmosphere could be deposited onto snow surfaces via condensation and scavenging (Gao et al., 2003; Goto–Azuma et al., 2001; Lee et al., 2008; Steinhauser et al., 2008, Wang et al., 2015; Zdanowicz et al., 2015). For example, Greenland and Antarctic snow and ice have recorded changes in the toxic trace element composition of the atmosphere arising from anthropogenic emissions (Bautron et al., 1991, 1998, Candelone et al., 1995; Hong et al., 1994, 1996; Schwanck et al., 2016). Snow also accumulates volcanic pollutants such as fluoride and aluminium (e.g. Flaathen and Gislason, 2007; Jaffe et al., 1994; Moune et al., 2006; Zreda−Grostynska et al., 1997). Melting of this polluted snow could lead to the release of toxic elements to aquifers and rivers.

The study of the Holuhraun lava formed during the 2014/2015 Bárðarbunga eruption also provides the opportunity to investigate the weathering rates of fresh basaltic material. Most newly formed volcanic lava in Iceland consists of basaltic glass, which is more reactive than crystalline basalt (e.g. Gislason and Eugster, 1987a; Gislason and Oelkers, 2003; Oelkers and Gislason, 2001; Gudbrandsson et al., 2014; Wolff−Boenisch et al., 2006). A number of studies have suggested that weathering rates depend on rock age, such that fresh basalts will weather faster than older basalts (e.g. Gislason et al. 1996; Jones et al., 2011; Navarre–Sitchler et al., 2007; White and Brantley, 2003; Wolff−Boenisch et al., 2006). The degree to which fresh basaltic lava exhibits accelerated weathering rates can be assessed by comparing catchment denudation rates before and after the eruption.

In this study we investigated the effect of the 2014/15 Bárðarbunga eruption on the chemical composition of the Jökulsá á Fjöllum river to complement the real time conductivity measurements performed by the Icelandic Meteorological Office (IMO). We report the river monitoring results and relate them to the seismic activity within the Bárðarbunga volcanic system (Sigmundsson et al., 2015). We investigated whether the river chemistry can be used as an indicator of impeding or ongoing volcanic activity. We also assess possible contamination of surface waters during the melting of volcanically polluted snow and predict its environmental consequences. Finally, we estimate the effect of newly formed lava on weathering rates within the catchment.

2. GEOLOGICAL SETTING OF STUDY AREA

The Bárðarbunga−Veidivötn volcanic system is located in the Icelandic Eastern Volcanic Zone. It is the second most active volcanic system currently in Iceland (Larsen, 2002; Thordarson and Larsen, 2007). It is approximately 190 km long and 28 km wide, covering an area of 2,500 km^2 (Thordarson and Larsen, 2007). It consists of two central volcanoes, the Bárðarbunga, and the Hamarinn, and a fissure swarm, including tens of kilometres of graben structures and up to 70 km long volcanic fissures. About one–third of this volcanic system lies beneath the Vatnajökull ice cap (Larsen and Gudmundsson, 2015). The Bárðarbunga central volcano has an 80 km^2 caldera rising to 2009 m a.s.l. Most of the eruptions have taken place within the ice–covered part of the volcanic system, emitting small to moderate volumes of basaltic tephra with an average magma volume of 0.04 km^3 (Dense−rock equivalent) and several have generated glacial floods (Thordarson and Larsen, 2007). Analysis of tephra layers deposited in the snow near Vatnajökull indicate that there were up to 330 hydromagmatic basaltic eruptions sourced from the Bárðarbunga central volcano and adjacent ice covered fissure swarms over the last 6,600 years, whereas there are no signs of either effusive or explosive eruptions at the margins of the central volcano (Larsen and Gudmundsson, 2015). The largest magma volumes, of more than 20 km^3, were produced during effusive basaltic eruptions from the ice–free part of the fissure swarm about 8,600 years ago (Larsen and Gudmundsson, 2015). The 2014/2015 Holuhraun lava, as indicated in Fig. 1, formed on the older Holuhraun lava field that erupted between 1794 and 1864 AD (Hartley and Thordarson, 2013). In the following text, the term ‘Holuhraun lava’ will refer to only the lava produced during the 2014/2015 Bárðarbunga eruption.

3. THE JÖKULSÁ Á FJÖLLUM RIVER

This study focuses in part on the chemistry of the Jökulsá á Fjöllum glacial river located in NE Iceland (Fig. 1). Due to its location, this river is expected to be the most affected by eruptions sourced from the Bárðarbunga volcano and the recently formed Holuhraun lava (Fig. 1a, b). The IMO has continuously monitored the discharge, water and air temperature, conductivity, and sometimes the water transparency at two stations on the Jökulsá á Fjöllum: the Upptyppingar and the Grímsstaðir (Fig. 1a). This data, and data from other rivers in Iceland that could be affected by volcanic eruptions and sudden glacial floods, can be viewed in real time on the web pages of the IMO (www.vedur.is; IMO, 2016) and are used for civil protection purposes (Galeczka et al. 2014; Jones et al., 2015). The bedrock in the Jökulsá á Fjöllum catchment predominantly consists of basaltic lavas and hyaloclastites (Eiriksdottir et al., 2008; Hards et al., 2000; Jóhannesson and Sæmundsson, 1998; Wood, 1976, 1978) with the average bedrock age of less than 0.8 million years (Gislason et al., 2006, Kardjilov et al., 2006). A large part of the catchment is located in the highlands and it is poorly vegetated (Kardjilov et al., 2006). The measured discharge at the Upptyppingar station ranges from 20 to 300 m^3/s whereas at the Grímsstaðir it ranges from 20 to

700 m^3/s (Kristmannsdóttir et al., 1999). Between the Upptyppingar and Grímsstaðir stations, several spring fed rivers and the glacier fed Kreppa river join the Jökulsá á Fjöllum. As shown by Kristmannsdóttir et al. (1999), the discharge at Upptyppingar usually accounts for 60% of the total discharge at Grímsstaðir. Several small glacial floods in the Kreppa river and rivers coming from the Brúarjökull glacier have also been observed in the Jökulsá á Fjöllum (Fig. 1a; Kristmannsdóttir et al., 1999). Taking account of the average flow velocity of the Icelandic rivers of 1.5 m/s (Gislason et al., 1996; IMO, 2015), it would take about 5–6 hours for water to flow from the Holuhraun lava field to Upptyppingar and about 12 hours to flow from Uppytppingar to Grimsstadir.

4. THE 2014/15 BÁRÐARBUNGA ERUPTION (August 31, 2014 – February 27, 2015)

Seismic activity beneath the Bárðarbunga central volcano had been increasing steadily since 2005, mostly in the northeast part of the caldera (IMO, 2015). Early in the morning of August 16, 2014 a seismic swarm began, starting the Bárðarbunga activity/unrest period referred to in text below. The seismic activity was caused by a lateral growth of a dyke intrusion towards the NE; it was measured to be at a depth of around 5–8 km (Sigmundsson et al., 2015). The lengthening of the dyke ended on August 27, around 10 km north of Vatnajökull, with a minor fissure effusive eruption in the Holuhraun lava field for about 4 h on August 29 (IMO, 2016; Sigmundsson et al., 2015). Two days later, a new eruption started from the same fissure and ended February 27, 2015. According to Sigmundsson et al. (2015), minor eruptions or leakage of magmatic heat may have occurred under Vatnajökull, as evidenced by shallow ice depressions marked by circular crevasses (ice cauldrons) discovered between August 27 and September 7. This eruption was gas−rich and ash−poor. The volume of tephra produced during this eruption was not substantial (Gudmundsdottir et al., 2015). The erupted lava, however, 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) making it the largest in Iceland since the 1783−1784 Laki eruption (Thordarson and Larsen, 2007). The erupted lava was a primitive olivine tholeite magma containing less than 1% phenocrysts (by volume) composed mainly of plagioclase and in minor amounts of olivine and clinopyroxene (Bali et al., 2014; Gudfinsson et al., 2015, Halldórsson et al., 2015). The total SO_2 emission to the atmosphere was estimated to be 11 ±5 Mt (Gislason et al., 2015). This emission caused anomalously high atmospheric SO_2 concentrations in Iceland and at several locations in Europe (Gislason et al., 2015). For comparison, the Laki eruption released 122 Mt of SO_2 (Thordarson and Self, 2003) whereas the global anthropogenic SO_2 emission in 2011 was estimated to be 101 Mt (Klimont et al., 2013). The total CO_2 and HCl emissions were calculated to be 6 and 0.1 Mt, respectively (Bali et al., 2015; Gislason et al., 2015; IMO, 2016). The gas flux during the first weeks of the eruption was estimated to be 719, 382, and 6.4 kg/s for SO_2, CO_2, and HCl, respectively, two to three times the average gas emission rates during the whole eruption period (Gislason et al., 2015). According to Icelandic Health Regulation (2002), the hourly average concentrations of SO_2 during as much as 20% of the eruption period, exceeded health limits of 350 $\mu g/m^3$ over almost all of Iceland (Gislason et al., 2015).

5. METHODS

5.1. Water samples

River water samples were collected from the Jökulsá á Fjöllum from August 16, 2014 to November 14, 2014 at incremental distances from its source, starting at the lava front, through the Upptyppingar and Grímsstaðir water monitoring stations (Fig. 1a). Conductivity and water temperature in the Jökulsá á Fjöllum were measured continuously by the IMO at Upptyppingar and Grímsstaðir (IMO, 2016). These parameters were also obtained *in situ* during the sampling. In most cases, spot samples collected at Upptyppingar and at the lava−front were taken into low−density 1L bottles and within several hours these samples were filtered through 0.2 µm Millipore cellulose acetate membranes into distinct bottles and/or vials as described below. Acid washed high−density polypropylene bottles or vials, were used to collect some samples for cation and trace metal analyses. Low and high−density polyethylene bottles or vials were used to collect samples for the other dissolved element measurements. Containers for dissolved nutrient analysis were acid washed with 1 M HCl. Water samples collected for major and trace metal analysis were acidified using Suprapur® 0.5 % (v/v) HNO_3. Amber glass bottles were used to collect filtered samples for pH and alkalinity measurements. Some samples were collected in high−density polyethylene buckets and poured into 2 L high−density polyethylene containers, which were sealed after they were filled completely. These water samples were filtered through 0.2 µm Millipore cellulose acetate membranes using a peristaltic pump, silicone tubing, and a 140 mm Sartorius® polytetrafluoropropylene filter holder. At least 1 L of sampled water was pumped through the filtration unit before the samples for analysis were collected.

5.2. Snow samples

Samples of fresh snow were collected in vicinity of the Bárðarbunga eruption site and lava field (Fig. 1b). Snow was sampled into low−density polyethylene heavy−walled 30−liter bags. These bags were washed with 1 M HCl then rinsed several times with DI water to remove all remaining ions prior to use. At each sampling site, 2−10 kg of snow was collected into the bags manually with hands covered with cleaned plastic bags to avoid snow contamination. Sampling bags were then packed into insulated boxes to ensure that the snow did not melt during their transport to the laboratory. Samples were kept in a freezer at −18 °C until they were melted by immersing the bags in 60 °C water for 20−40 minutes depending on snow volume. Once the snow was melted, the melt water was immediately filtered and processed similar to the river water samples as described in section 4.1. Four snow samples enriched in fresh tephra (J−M; Fig. 1b) were collected into the plastic bags using a stainless steel shovel. Because of possible contamination, these samples were analysed only for major anions and cations concentrations as the trace and heavy metals could originate from the sampling tools. In addition, some of these snow samples partially melted during their transport to the laboratory. These samples will serve as an example of the melted snow chemical composition affected by tephra interaction.

5.3. Osmotic samplers

Two osmotic samplers were deployed in the Jökulsá á Fjöllum close to the Grímsstaðir and Upptyppingar monitoring stations (Fig. 1a) for daily monitoring of the river chemical composition. These osmotic samplers were custom built by the Sensors Development Group at the University of Southampton and Quayside Precision Engineering, Southampton; these are similar to those used previously by Gkritzalis−Papadopoulos et al. (2012a, 2012b), Jannasch et al. (2004), and Jones et al. (2015). These samplers are equipped with osmotic membranes, which enable collection of surface water samples continuously in the field. These osmotic samplers are described in detail by Jones et al. (2015).

5.4. Chemical analysis

A variety of methods were used to analyse the water and melted snow samples. The pH of the river samples was determined within 48 hours after sampling using an Oakton pH electrode. The pH of melted snow was measured in filtered samples several hours after its melting using the same electrode. The pH of non–diluted samples from the osmotic sampler was measured using a Thermo Scientific Orion Micro Electrode. The dissolved inorganic carbon (DIC) in most of the water samples was quantified from measured pH and alkalinity using the PHREEQC 2.17 geochemical code (Parkhurst and Apello, 1999). Alkalinity was determined by standard titration; the end point of this titration was determined by the Gran function. In the case of osmotic samples, snow samples, and small volume river samples, the DIC was measured together with the anions F, Cl, SO_4 using an IC−2000 Dionex, ion chromatograph (Dionex, 2006). The dissolved S_2O_3 and SO_3 were determined in samples collected at the lava front using this IC−2000. Cations and trace metals were measured using the Icelandic Science Institute Spectro Cirus Vision inductive coupled plasma, optical emission spectrometer (ICP−OES; Spectro Ciros Vision, 2005), calibrated with an in–house standard and verified against the SPEX Certified Reference Standard. Several river water and snowmelt samples were also analysed by inductive coupled plasma atomic emission spectrometer and inductive coupled plasma sector field mass spectrometer ICP−SFMS at ALS Scandinavia, Luleå, Sweden. Samples for dissolved PO_4, NO_3, NO_2, and NH_4 were collected in high−density polypropylene vials and kept frozen until their colorometrical determination using an Alpkem AutoAnalyser. Samples for nutrient determination were refrigerated at a temperature of −18 °C within several hours after collection and kept frozen until analysis. Analytical measurements had an inter−laboratory reproducibility within 5.0 %.

5.5. Discharge measurements

Discharge at the Upptyppingar and Grímsstaðir monitoring stations was calculated by the Icelandic Meteorological Office using a rating curve describing the relationship between water level and discharge (IMO, 2016). Water level was continuously measured and recorded at 60 minute intervals. To validate the rating curve, which depends on the stability of the river bed cross section, the discharge was measured several times each year at each station. If the river water level at the measuring site is influenced by the presence of ice, river discharge is estimated by taking into account the air temperature, precipitation, and discharge of nearby ice−free rivers (IMO, 2015).

5.6. Fluid saturation state and mixing calculations

Aqueous speciation, charge balance, DIC, and mineral saturation states of water and melted snow collected during this study were calculated using the PHREEQC 2.17 geochemical code (Parkhurst and Apello, 1999) together with the *phreeqc.dat* database updated with the aqueous complex formation and mineral solubility constants reported by Gysi and Stefánsson (2011). These calculations were performed using the measured samples compositions, pH, and water temperature summarized in Tables 1, 2, 3, and 4.

To simulate the chemical reactions occurring when contaminated melted snow comes into contact with surface waters, modelling calculations were run mixing the most contaminated snow (snow D) with increasing proportions of (1) water from the Fjarðará river, and (2) water from Jökulsá á Fjöllum at Upptyppingar (Table 1ES in Electronic Supplement). These rivers were chosen because of their close proximity to the eruption site, their distinct alkalinity, and therefore pH buffering capacity. The Fjarðará river waters have low alkalinity and therefore a low pH buffering capacity, whereas the Jökulsá á Fjöllum waters have a relatively high alkalinity and therefore a high pH buffering capacity. Laboratory and field experiments show that the very first melt water fraction may contain more than five times more impurities than the average snowpack concentration (Gislason, 1990; Johannessen and Hendriksen, 1978). Consequently, the proton and ion concentrations may be higher in the very first melt of the polluted snow compared to the bulk snow. As a result, the modelling included mixing of the most polluted snow D concentrated by a factor of five.

5.7. Weathering rate calculations

The effect of the presence of fresh basalt on weathering rates was characterised in this study by comparing Na denudation rates in Jökulsá á Fjöllum catchment before and after the eruption. Sodium was chosen for this calculation as it is negligibly incorporated into secondary phases. The Na denudation rates before the eruption were calculated from the Na concentrations and instantaneous discharge measured at the Grímsstaðir monitoring station during 1998–2001. An equation correlating instantaneous Na flux versus instantaneous discharge was generated. The term ‘flux’ in this case corresponds to the mass of material transported in dissolved form by the river water towards the oceans. A corresponding correlation curve was generated from the Na flux versus discharge during the August–November 2014 monitoring period. Comparison of these two correlation curves was used to quantify the effect of the presence of fresh lava and volcanic gases on catchment weathering rates.

6. RESULTS

6.1. Water samples collected at the lava front

Chemical compositions of the water samples collected near the lava front are listed in Table 1 and 2. The water samples had *in situ* pH values ranging from 6.34 to 8.19 and conductivity from 10.2 to 299.0 µS/cm. Water samples 14–JF–5 to 14–JF–7, presented in Fig. 2, were collected during a single sampling campaign. Sample 14–JF–5 was collected upstream from the lava front, whereas other two were collected at the lava front. The temperature of these waters samples increased from 7.6 °C upstream to about 40 °C downstream from the lava front, whereas the corresponding measured 22 ºC pH decreased from 6.93 to 6.48, and the corresponding conductivity increased from 10.2 to about 30 µS/cm. As can be seen in Fig. 2, the fluid anion concentrations increased by factors of 114 for F, 71 for SO_4, and 7 for Cl, when passing over this lava front. Similarly, the cation concentrations increased over this distance by factors of 7 for Mn; 5 for Na and Co; 3 for K, Ni, Sr, and P; 2 for Zn, Ba, SiO_2, Mg, Ca, Li, and V; and slightly more than 1 for Cu, Al, V, Ti, and Fe. In contrast, the DIC concentration of the water samples decreased by a factor of three in samples 14–JF–6 and 7 compared to 14–JF–5. Dissolved SO_3^{2-} was also detected in samples 14−JF−6 and 14−JF−7 immediately after their collection.

Most of the other water samples collected at the lava front had higher temperatures than normal Icelandic surface waters and ranged up to 41 ºC; typical Icelandic surface waters do not exceed 10 ºC (Eiriksdottir et al., 2013ab). The conductivity of water interacting with the lava was up to 299 µS/cm (Table 1). These waters were also enriched in SO_4, Cl, and F compared to waters collected at the Upptyppingar monitoring station. The average SO_4 concentration in the Jökulsá á Fjöllum waters at the Upptyppingar station after the newly formed lava flowed into the main channel of Jökulsá was 127 µmol/kg, whereas the highest SO_4 concentration obtained at the lava front was 948 µmol/kg. Similarly, the average F concentration at Upptyppingar after the lava flowed into the main channel of the Jökulsá was 12.3 µmol/kg, whereas at the lava front, the F concentration was up to 199.0 µmol/kg. Similar enrichments were observed in major and trace cations concentrations including Al, Fe, Mn, and Sr. The spring water used to quench a molten lava sample (called experimental water in Table 1) was collected and analysed for major anions and cations, and compared with the background concentrations. This water was characterised by a lower DIC but increased SO_4, F, and Cl compared to the background water. In addition, the conductivity and cation concentrations were higher compared to background water (Table 2).

6.2. The chemistry of Jökulsá á Fjöllum waters at Upptyppingar and Grímsstaðir

6.2.1. Spot samples

There were two Jökulsá á Fjöllum monitoring periods in this study, one before (18.8.2015–7.9.2015) and one after (7.9.2015–27.11.2015) the lava flowed into the main river channel. There was no continuous conductivity monitoring at Upptyppingar due to failure of the *in situ* monitoring system. Spot conductivity measured before the lava flowed into the main Jökulsá channel decreased with discharge, whereas afterwards the conductivity increased with discharge. At Upptyppingar, most elemental concentrations decreased with time during the entire sampling period, whereas the

SiO_2, F, SO_4, P, V concentrations increased. The Al, Fe, and Ti concentration patterns were time independent.

The average charge imbalance of all the analysed spot samples collected at Upptyppingar and Grímsstaðir during the whole monitoring period was 2.2%. The highest charge imbalance was calculated for sample 14–JF–2–3 and it equalled 4.9%. The highest discharge measured at the Upptyppingar station during the sampling period was 240 m^3/s on September 2, 2014 at 23:00 GMT, whereas the highest at Grímsstaðir was 350 m^3/s measured on August 24, at 13:30 GMT. The average measured water temperature was 4.5 and 5.4 °C, and the calculated *in situ* pH (pH at the water temperature measured during sampling; see Table 1) of the samples ranged from 7.11 to 8.18 and from 7.97 to 8.37 at Upptyppingar and Grímsstaðir, respectively. The average conductivity measured at Upptyppingar was higher than at Grímsstaðir. At the Upptyppingar monitoring station the average major cation and anion concentrations were higher than corresponding concentrations at Grímsstaðir by factors of 1.1 to 1.7. The average concentrations of Fe, Al, and Ti were higher at Grímsstaðir compared to Upptyppingar by factors of 1.8, 1.7, and 1.7, respectively. Although there were no major differences between the element concentrations at Upptyppingar before and after the lava flowed into the main Jökulsá channel, the relation between element concentrations and discharge at Upptyppingar and Grímsstaðir was different (see Fig. 3, 4 and Fig. 1ES in Electronic Supplement). Before the lava flowed into the main channel of the Jökulsá á Fjöllum, major element concentrations at Upptyppingar decreased with increased discharge (Fig. 3). In contrast, however, Al and Fe concentrations increased with increased discharge. A distinct pattern was observed after the lava flowed into the main channel of the Jökulsá: all concentrations but SiO_2, SO_4, F, and V increased with increasing discharge (see Fig. 4). At Grímsstaðir before the lava came into the main Jökulsá channel, increasing concentrations of major ions and trace metals with increasing discharge were observed (Fig. 1ES in Electronic Supplement). In contrast Al, Fe, and Ti concentrations decreased with discharge.

6.2.2. Waters collected by the osmotic samplers

Osmotic samplers were deployed twice during the monitoring period, first during August and September 2014 at Grímsstaðir and second during October and November 2014 at Uppytppingar. The chemical composition of waters collected by the osmotic sampler at Grímsstaðir is shown in Fig. 5. The chemical composition of waters collected at Upptyppingar is presented in Fig. 2ES in the Electronic Supplement. Water samples collected at the Upptyppingar station were alkaline with a pH ranging from 7.1 to 7.7. Note that the pH of the osmotic water samples collected at Grímsstaðir was not determined. The averaged calculated TDS was 83 and 95 mg/kg for the Grímsstaðir and Upptyppingar samples, respectively.

Concentrations of SO_4, Cl, DIC, major cations, and some trace metals (Fe, Al, Sr) decreased with increased discharge at Grímsstaðir before the lava flowed into the main channel of Jökulsá (Fig. 3ES (a,c,e) in Electronic Supplement. The F concentration was independent of discharge. After the lava flowed into the main river channel, the discharge dependence of the concentrations changed:

the anions and all major cations other than SiO_2, and Fe, and Al slightly increased with discharge (Fig. 3ES (b,d,f) in Electronic Supplement). At Upptyppingar during the osmotic sampler deployment, most element concentrations increased with discharge. The Al and F concentrations were independent of discharge (Figs. 4ES−7ES in Electronic Supplement).

6.3. Snow samples

The weight of collected snow samples, including imbedded sediments and aerosols, was 0.7 to 7.65 kg. The concentration of sediments including tephra produced during this eruption and recovered after melting and filtering the melted snow was up to 170 g/kg, but mostly below 10 g/kg (Table 3). The contact time between meltwater and the sediment during melting at ~ 0 °C was short, 20−40 minutes. The chemical composition of the snow samples collected near the lava front at the time of sampling can be seen in Tables 3 and 4 and Fig. 6. The *in situ* (0.1 °C) pH and conductivity ranged from 3.34 to 4.98 and 5.6–234 µS/cm, respectively (see Fig. 6). Trace element concentrations in the snowmelt were higher than in water collected at the lava front. Note that the trace metals measured in the melted snow samples J−M were not considered due to the sampling procedure as described in section 4.2.

6.4. Saturation state of the water and melted snow samples

Saturation state calculations indicate that the waters collected from Upptyppingar, Grímsstaðir and the lava front were undersaturated with respect to calcite and other Ca−Mg−carbonates. The partial pressure of CO_2 was higher than atmospheric in river samples collected at Upptyppingar and Grímsstaðir, whereas, it was lower in the waters collected near the lava front. The water samples were mostly supersaturated with respect to the less soluble Al−bearing secondary phases including gibbsite, imogolite, kaolinite, and Ca−montmorillonite. Water samples collected at Upptyppingar and Grímsstaðir were supersaturated with respect to zeolites (stilbite, heulandite, and chabazite) and Fe bearing phases including amorphous goethite, goethite and amorphous $Fe(OH)_3$. Waters collected at the lava front were mostly undersaturated with respect to zeolites but supersaturated with respect to crystalline Fe–phases. The melted snow samples were highly undersaturated with respect to all of these phases.

7. DISCUSSION

7.1. Waters collected from the lava front

Dissolved CO_2 dominates the alkalinity of neutral and alkaline Icelandic glacial river waters under normal conditions (e.g. Gislason et al., 1996; Oskarsdottir et al., 2011). The bedrock and suspended material is mostly comprised of rapidly dissolving basalt that increases fluid pH, conductivity, and DIC in surface waters (Gislason and Eugster 1987a,b). In general, the conductivity and DIC of water samples collected at the lava front are relatively low compared to the Jökulsá á Fjöllum waters at the Upptyppingar and Grímsstaðir monitoring stations (Table 1 and 2). In addition these waters contain considerable SO_4, Cl, and F, indicating substantial dissolution of magmatic gases during water–lava–gas interaction. Note that SO_2, HF, and HCl gases are more soluble in water than is CO_2. The addition of the volcanic SO_2 into the waters and snow is indicated by the DIC/SO_4 ratio. Figure 7 presents the DIC/SO_4 ratio in all collected water and snow samples at different stages of the Bárðarbunga unrest. The highest ratio of 85 was measured in water collected near the eruption site, upstream from the lava. This water originally likely contained high carbon alkalinity due to water−rock interaction during subglacial chemical weathering. As soon as the lava interacted with this water, the DIC/SO_4 ratio decreased to almost 0. This observation suggests that volcanic gases such as SO_2 dissolve in water, dissociate, and titrate out the dissolved carbon alkalinity. In samples collected downstream from the lava, the total dissolved SO_4, SO_3^{2-}, Cl, and F accounted for 80 % of the total anion budget. In addition, the major cation concentrations increased by factor of 2 for SiO_2, Ca, and Mg, 5 for Na, and 4 for K in these samples. There was no major increase in Fe and Al concentrations, however, Mn and Sr increased by factors of 5 and 2, respectively. This indicates that these metals originated mainly from rock dissolution rather than from metal salts. The rise in water temperature at the hot lava front increased basalt dissolution rates enhancing element release (e.g. Gislason and Oelkers, 2003). The presence of the aqueous SO_3^{2-} species confirms directly the interaction of volcanic SO_2 gas with the water (Lelieveld, 1993; Mehta, 2010). The water that quenched the molten lava (14−JF−12; Table 2) was enriched in dissolved SO_4 and F by factors of 4 and 11 compared to the background sample (Table 2), whereas there was almost no increase in Cl. This indicates that the direct water–lava interaction delivered mainly F and SO_4 into the water. The lack of an increase in Cl might be attributable to its earlier degassing at the eruption vent (e.g. Gislason et al., 2015). Other water samples collected from the ponds close to the lava front were also enriched in SO_4 and F. In addition, dissolved SO_4 and F in these waters were concentrated than in the Jökulsá á Fjöllum river at Upptyppingar during the eruption monitoring period, indicating that SO_4 and F were sourced from lava−water interaction and subsequently diluted downstream.

6.2. Controls on water chemistry at Upptyppingar and Grímsstaðir during the initial stage of eruption

6.2.1. Concentrations versus discharge

During the normal stage of the Jökulsá á Fjöllum, when it is not affected by volcanic activity, decreased conductivity is observed with rising discharge, as rainfall or enhanced glacial/snow melting dilutes the water (e.g. Eiriksdottir et al., 2013a,b). During glacial floods, however, increased conductivity is observed with increased discharge; this observation frequently indicates that a flood is impeding (e.g. Galeczka et al., 2014a, 2015; Gislason et al., 2002; Kristmannsdóttir et al., 1999). High conductivity and discharge often indicates intensified volcanic or geothermal activity in the rivers draining this area. Monitoring of the glacial rivers draining Vatnajökull and Mýrdalsjökull has shown that the chemical composition of these rivers varies seasonally, and even daily, in response to glacial melting (Eiriksdottir et al., 2013a,b; Gislason et al, 2004a,b; 2007;

Kristmannsdóttir et al., 2006). The conductivity of the Jökulsá á Fjöllum waters at Uppytppingar and Grímsstaðir over last several decades and during the Bárðarbunga unrest is plotted as a function of discharge in Fig. 8. The background values were taken from Gislason et al. (2004a) and Kristmannsdottir et al. (2006). As can be seen, the conductivities measured during this study were within the range measured in the absence of volcanic activity. In addition, the data provided by Krismannsdottir et al. (1999) show that during the typical summer glacial floods in the Jökulsá á Fjöllum, higher conductivities are sometimes observed than that measured during the 2014 Bárðarbunga activity; there was no major change in the river conductivity during the whole period of Bárðarbunga volcanic activity. A major change was observed when newly formed lava flowed into the main channel of the Jökulsá á Fjöllum, when a contrasting pattern of rise in conductivity and dissolved element concentrations with increasing discharge was observed (Fig. 3, 4, and 3ES in Electronic Supplement). The background conductivity in the Jökulsá á Fjöllum waters, measured during 1998–2001 at Grímsstaðir, decreased with increasing discharge as commonly seen in Icelandic glacial rivers (Eiriksdottir et al., 2013a, b). This pattern was observed at Upptyppingar before lava flowed into the main channel of the Jökulsá. During the eruption, when lava flowed into the Jökulsá channel, conductivity increased with discharge reflecting the inflow of more concentrated waters into the river. Enhanced water–rock interaction due to higher temperature and the addition of volcanic gases likely drives the increased element concentrations in the water. Outflow of spring waters often occurs at the Holuhraun lava field due to the presence of a shallow groundwater system in front of the glacier. The weight and heat of newly formed lava might have increased the outflow from these springs, as these factors could increase subsurface water pressure. Increased concentrations of a number of elements including DIC and B with increasing discharge confirm enhanced rock dissolution. Boron is considered to be a conservative element in Icelandic natural waters and is an indicator of water–rock interaction (Arnórsson and Andrésdóttir, 1995). Increased dissolved F concentration might also have enhanced suspended matter and bed rock dissolution and lead to the elevated carbonate alkalinity measured during the early stage of Bárðarbunga activity (Fig. 4ES in Electronic Supplement; Harouiya and Oelkers, 2004; Wolff−Boenisch et al., 2004). Similar patterns of increased element concentrations with increasing discharge was observed following the flow of lava into the main channel of the Jökulsá by osmotic sampling at the Grímsstaðir station, but it was less evident as the Jökulsá á Fjöllum at Grímsstaðir is diluted by a factor of ~3 by with spring waters compared to that at Upptyppingar (Kristmannsdóttir, et al., 1999). Although it may be possible to use increased river water SO_4, F, and Cl concentrations (Fig. 5ES−7ES in Electronic Supplement) to predict upcoming volcanic activity, such signals are not sufficiently large to be unambiguous.

7.2.2. Alkalinity development

The typical alkalinity of Icelandic glacial rivers is ~0.5–1.5 meq/kg (Gislason et al. 2009; Eiriksdottir et al., 2013ab, Oskarsdottir et al., 2011). This alkalinity results from water–suspended particle interaction and water–bedrock interaction. The high alkalinity measured in rivers in the Icelandic volcanic rift zone originates from the fast dissolution rates of young rocks and magma degassing into groundwater aquifers (Gislason et al., 1996; Oskarsdottir et al., 2011). The annual magmatic CO_2 flux from volcanoes and geothermal systems in Iceland has been estimated to be 1−2 million tonnes/year (Arnórsson and Gislason, 1994). Most of the magmatic CO_2 is lost during quiescent degassing rather than during volcanic eruptions (e.g. Aiuppa et al., 2004; Federico et al., 2002). Ilyinskaya et al. (2015) estimated that <15% of the discharged gas reaches the summit of Icelandic Hekla volcano during the non−eruptive period; the rest is dissolved into groundwater. Increased concentrations of dissolved SO_4, Cl, and F in Icelandic rivers are often indicators of impeding or ongoing volcanic activity. Before the eruption at Holuhraun lava field, at the early stage of Bárðarbunga activity, the DIC and alkalinity concentrations were higher than previously measured at the Upptyppingar station, and at the upper range of values obtained at the Grímsstaðir station (see Fig. 4ES in the Electronic Supplement). During the eruption, the conductivity measured in the Jökulsá á Fjöllum at both stations did not show a clear volcanic activity signal, however changes in DIC and SO_4 concentrations suggested a considerable effect of volcanic activity on water compositions (see Fig. 5). The DIC/SO_4 ratio was relatively high at the beginning of the Bárðarbunga activity until the lava reached the main channel of the Jökulsá á Fjöllum on September 7, 2014, when this ratio decreased indicating the dissolution of acidic gases into this river water (Fig. 7). Similarly, a low DIC/SO_4 ratio was observed in the water collected at the lava front as described in section 6.1. This indicates that the effects of lava−water interaction were observed in the river channel. Although the Jökulsá á Fjöllum at the Upptyppingar and Grímsstaðir stations is characterized by a relatively high alkalinity, the addition of volcanic acids was sufficiently strong to affect the sampled water chemical composition. In addition, although the conductivity during whole monitoring period was unaffected, the DIC/SO_4 ratio changed, indicating that the conductivity does not fully reflect the processes occurring during the volcanic unrest. Increased water–rock interaction caused by intensified seismic activity might explain the increase in measured alkalinity and DIC concentrations at the initial stage of the Bárðarbunga unrest, before the lava flowed into the main channel of the Jökulsá; seismic activity could enhance water−rock interaction by opening up new flow paths and thus exposing new mineral surfaces to reactive acidic fluids. In addition tectonic activity might have enhanced the magmatic CO_2 input into the groundwater recharging Jökulsá a Fjöllum resulting in increased DIC concentration.

The concentrations of SO_4, and F in the Jökulsá á Fjöllum at Uppyytppingar throughout the early stage of the Bárðarbunga unrest, before the eruption at the Holuhraun lava field, were higher than background concentrations, but they were close to the upper range of values measured at Grímsstaðir (Figs. 5ES−7ES in Electronic Supplement). Before the onset of the Bárðarbunga eruption, at 11:20 GMT on August 23, 2014, a seismic tremor indicated that an eruption beneath Dyngjujökull glacier occurred (IMO, 2016). This would most likely result in melt water entering the Jökulsá á Fjöllum. During this period, two or three cauldrons formed SE of the Bárðarbunga caldera associated with a possible subglacial eruption. The estimated volume of the cauldrons was up to $20x10^6$ m^3 (Reynolds et al., 2015). The chemical compositions of the water collected by the osmotic sampler during August and September at Grímsstaðir and spot samples collected at Uppytppingar and Grímsstaðir showed no major discharge or conductivity increase on August 23 or shortly thereafter. In addition, the anion concentrations of the continuous samples collected at Grímsstaðir were within the range measured during the entire initial stage of the Bárðarbunga unrest. Osmotic sampling at Upptyppingar during October/November shows an increased concentration of major anions with increasing discharge, confirming the inflow of more concentrated water into Jökulsá (Fig. 4ES–7ES in Electronic Supplement), however, no major short–term changes in chemical composition (DIC/SO_4 ratio, SO_4, Cl, F concentrations) were observed. This suggests that apart from Holuhraun lava−water interaction, there were no additional subglacial eruptions affecting Jökulsá chemical concentrations, during this period. If such eruptions however occurred, the chemical signal in sampled waters was not affected by these events.

7.3. Snow samples

Melted snow samples collected near the eruption vents were characterized by a strong inverse dependence of SO_4, Cl, and F concentrations on pH, indicating that volcanic salts such as those originating from volcanic gases, such as SO_2, HCl and HF, acidified the snow (Fig. 6). According to Graedel and Franey (1975), because of its relatively large surface area, snow can scavenge more pollution from air than rain droplets. Based on the composition of the background snow sample A, the contribution of the sea spray Cl is estimated to be less than 5.15 µmol/kg (Table 4). In the melted snow samples having the lowest pH, samples D and H, SO_4 and Cl dominated the charge balance as showed by the milliequivalents plots illustrated in Fig. 9. Unpolluted melted snow collected at the Langjökull glacier in western Iceland during 1997–2006 had an average pH of 5.7, with the lowest pH of 5.25 at ambient laboratory temperature and average concentrations of 3.5, 77.7, and 0.1 µmol/kg for SO_4, Cl, and F, respectively (Gislason et al., 2000). These concentrations are 30, 3, and 961 times lower than the average concentrations of these anions measured in the melted snow samples collected during this study. The concentration ratio of selected elements relative to Cl in the melted snow collected close to Holuhraun lava and Langjökull are shown in Fig. 10. These ratios indicate that the snow samples collected near Holuhraun were enriched in SO_4 and F. In addition, the concentrations of Al, Na, and Fe, were higher than that of unpolluted snow, where marine aerosols are the primary source of these cations. Given the presence of tephra in the snow samples, dissolved halogen and metal concentrations might have partly originated from dissolution of salts formed on this tephra (e.g. Bagnato et al., 2013; Olsson et al., 2013). There was no major increase in the main rock forming constituents such as SiO_2 other than in snowmelt samples J and K, but most metals exhibit a positive linear correlation with anions suggesting that these elements were degassed at depth and transported in the gas phase as chlorides, fluorides and/or sulphate salts/aerosols (e.g. Moune et al., 2006). Note that the Cl, F, and S concentrations in bulk basalts are low (e.g. Oskarsson et al. 1981) and therefore dissolution of basaltic tephra would not account for their high concentrations in those snow samples. The concentration of SiO_2 was relatively high in snow samples J and L where considerable amounts of tephra interacted with partly melted snow for several hours. In contrast, snow samples A to I, N, and O were melted in the laboratory and therefore the chemical composition of this snow was unaffected by tephra dissolution. The pH of samples J and L was slightly higher than expected considering the anion concentration, possibly due to fluid neutralization by tephra dissolution. There was no intermediate sulphur species measured in the snow samples, indicating that SO_2 oxidized to SO_4 before snow deposition. As can be seen in Fig 9, protons balanced about half of the negatively charged anions in most polluted samples; the rest was balanced by water soluble salt and/or aerosols' metals such as Al (mainly as sulphates), Fe, Na, Ca, and Mg (as chlorides).

The molar S/Cl ratios of the melted snow samples are different from that measured in the gas plume. According to Gislason et al. (2015), the integrated SO_2 emission rate, based on petrological estimates, was 700 kg/s, whereas the HCl flux was 37 kg/sec, and HF was below the detection limit of the petrologic measurement. Based on these estimates, the average molar S/Cl ratio of the gas flux was approximately 7. In contrast, the snow affected by the eruption had an average ratio of 0.9, whereas ratio in water at the lava front was 12. The Cl enrichment in snow compared to the water at the lava front and the overall gas flux may be related to its early degassing at the volcanic vents. Note also that the solubility of HCl is higher than that of SO_2 at the high pH of the snowmelt waters, which could also lower S/Cl ratios.

The concentrations of F, Al, Fe, Mn, and Cd in some melted snow samples collected near the Holuhraun eruption site exceeded the European Commission drinking water standards (European Communities, 2008). In addition, Cu and Pb were higher than standards established by the Icelandic directive for surface waters, defining limits to protect sensitive biota, Category III (IcD, 1999). The melting of polluted snow during the spring might, therefore, adversely affect surface water chemical compositions, vegetation, and aquatic biota (e.g. Flaathen and Gislason, 2007). In addition to the high toxic element concentrations in the polluted snow (Fig. 6, Table. 4), enhanced dissolution of bedrock and/or suspended material caused by acidic snowmelt might further increase these concentrations. Aluminium is of major concern due to its detrimental effect on aquatic life (Brown et al., 1982; Dietrich and Schlatter, 1989; Freda et al., 1991; Gensemer and Playle, 1999; Ikuta et al., 2001; Leivestad and Muniz, 1976; Playle and Wood, 1990; Poleo, 1995; Staurnes et al., 1993). In addition, dissolved F sourced from volcanic gases will enhance basalt dissolution rates (Wolff–Boenisch et al. 2004). In acid solutions at pH of 5.5, fluoride becomes phyto−available through aqueous complexation as soluble aluminium−fluoride compounds (Stevens et al., 1997); there is evidence of increased F uptake by animals via the uncharged inorganic Al−complex AlF_3 (Klein, 1995; Varner et al., 1998; Kausz et al., 1999; van der Voet et al., 1999; Strunecka and Potocka 1999). As can be seen in Fig. 9, polluted snow contained considerable concentrations of different Al species, which contributed up to 15% of the dissolved ion budget.

6.4. Mixing of snowmelt with surface waters

Geochemical calculations were performed to assess the potential river water contamination risk associated with the melting of polluted snow. The risk associated with mixing polluted snow with surface waters depends on the chemical composition of the surface waters. For example, rivers having low alkalinity (low buffering capacity) such as those draining old bedrocks in East Iceland (e.g. Eiriksdottir et al., 2013 a, b; Louvat et al. 2008) will be more sensitive to pH changes upon mixing with acidic snowmelt waters. Rivers with high buffering capacities, such those draining Icelandic rift zones, will be less affected by the interaction with acidic snowmelt waters. For a worst case scenario, initial melted snow element concentrations were assumed to be five times higher than the average melted snow composition measured in this study (see Johannessen and Henriksen, 1978). This snow was mixed in model calculations with different proportions of 1) low alkalinity Fjarðará river water, and 2) high alkalinity Jökulsá á Fjöllum river water (e.g. Eiriksdottir et al., 2013a; Gislason et al. 2009; Kristmannsdóttir et al., 1999). Results of these calculations, shown in Fig. 8ES in Electronic Supplement, indicate that after diluting the snow with Fjarðará river water by a factor of 35, the melt water pH was predicted to rise from an initial 3.5 to 6.6, and it became slightly supersaturated with amorphous $Al(OH)_3$. Precipitation of aluminium hydroxides will lower the dissolved Al concentrations and potential scavenge some toxic metals. After diluting snowmelt with Upptyppingar river waters by a factor of 4, the pH rose to 6.9 and amorphous $Al(OH)_3$ was predicted to precipitate. This modelling confirms that low alkalinity surface waters such as numerous salmon rivers in East Iceland will be more affected by polluted snowmelt than those with high alkalinity and therefore dedicated monitoring should be considered to protect these fish habitats during volcanic activity.

6.5. Elemental fluxes and weathering rates

The elemental fluxes within the Jökulsá á Fjöllum catchment at Grímsstaðir during 1998−2001 and during the 2014 Bárðarbunga activity are shown in Fig. 11. This catchment was chosen in this study for several reasons; (1) the Jökulsá á Fjöllum river was the most affected by the Bárðarbunga unrest and eruption at the Holuhraun lava field, (2) it has been intensively studied in the past resulting in availability of chemical data collected over long period of time (Gislason et al., 2009), and (3) continuous monitoring of Jökulsá á Fjöllum at Grímsstaðir carried out by the IMO provides discharge measurements which can be used for fluxes and denudation rates calculations.

As can be seen in Fig. 11, dissolved fluxes increased considerably during the 2014 Bárðarbunga activity comparing to the 1998−2001 monitoring period. The most affected dissolved constituents were Na, SiO_2, Mg, Fe, and Al. Note that most of the trace metals measured in samples collected by the osmotic sampler at Grímsstaðir were below detection limit and therefore fluxes could not have been calculated from these measurements. The Fe and Al flux increased by order of magnitude during the Bárðarbunga activity compared to background fluxes. The Fe, Al, and SO_4 fluxes were slightly higher after the lava flowed into the main channel of Jökulsá (see ‘Grímsstaðir after’ on Fig. 11) compared to the earlier measurements (see ‘Grímsstaðir before’ on Fig. 13). The DIC flux was lower after the lava flowed into the Jökulsá, confirming the removal of carbon by the addition of volcanic H_2SO_4. The increase of dissolved fluxes during the volcanic activity might have some positive effects on biological activity as an increase in Fe flux will promote nitrogen fixation and therefore primary productivity at the coast line in cases where Fe is a limiting element (White, 1999). Similarly, an increase in SiO_2 flux could enhance diatoms growth. As reported by Ólafsson and co-workers (2008) diatoms consume most of the dissolved silica in the coastal waters of southwest Iceland during the early spring.

Chemical denudation comprises of a number of processes including numerous dissolution and precipitation reactions. To simplify this process as much as possible we focussed on the chemical denudation rates of sodium. Sodium is considered as one of the most mobile major element during the chemical weathering of Icelandic basaltic terrains since it is released from primary minerals and glasses but not readily incorporated into secondary minerals (Gislason et al., 1996; Eiriksdottir et al., 2008; 2013c). In addition, there is little contribution to sodium denudation from secondary minerals such as zeolites. During the Bárðarbunga activity, the average Na flux was 4.5 kg/s whereas the background Na flux (1998−2001) was estimated to be 1.9 kg/s. The average annual dissolved Na flux during the 1998−2001 was estimated to be 57,615 tonnes from the trendline obtained for the 1998−2001 data (see Fig. 11). Using this same trendline the 2014 flux would have been 59,674 tonnes. Using the trendline curve obtained during the 2014 monitoring period (Fig. 11) the 2014 Na flux was calculated to be 79,793 tonnes, which is 24% higher than that estimated from the pre−Bárðarbunga activity data. This is significant as only 1% percent of the catchment was covered by fresh lava at the end of September 2014. The former Na flux corresponds to about 4.0×10^6 tonnes of rock whereas the latter to 5.4×10^6 tonnes of rock, calculated based on Na concentration of Stapafell basaltic glass (Gislason and Oelkers, 2003; Galeczka et al., 2014b). The Na flux during the 2014 August/September Jökulsá at Grímsstaðir monitoring determined from osmotic sampler waters was 1.77 times higher than during the corresponding period of 1998−2001. This corresponds to 3.4×10^5 tonnes of rock, which had to dissolve to account for this difference. This mass equals approximately 0.01% of the mass of lava erupted during this activity.

The cause of the observed increased chemical denudation rates during and following the volcanic activity is challenging to constrain. Although, it has been argued that fresh, young basalt exhibit faster chemical weathering rates than corresponding older rocks (e.g. Gislason et al. 1996; White and Brantley, 2003; Navarre–Sitchler et al., 2007; Jones et al., 2011), other factors could contribute. For example, the volcanic activity increased SO_4, Cl, and F fluxes to the surface waters, as well as decreased pH. Each of these factors also tend to increase the dissolution rates of basalt and its mineralogical constituents (Flatthen et al., 2010; Gislason and Oelkers, 2003; Oelkers and Gislason, 2001; Wolff−Boenisch et al., 2004;).

7. CONCLUSIONS

This study quantified the effect of volcanic activity and arrival of fresh lava during the 2014/15 Bárðarbunga eruption on the local surface water chemistry and rock reactivity. The dissolution of volcanic gases increased the SO_4, F, Cl concentrations of surface waters by up to two orders of magnitude during lava−gas−water interaction decreasing the dissolved carbonate alkalinity. These chemical changes and the presence of fresh lava increased the average chemical denudation rate, calculated based on Na flux, within Jökulsá á Fjöllum catchment by a factor of two compared to the background flux. Moreover, snow was found to concentrate acidic volcanic gases during the eruption. The eventual melting of this snow will release the gas constituents in dissolved form to the local rivers increasing the risk of possible acidification of the surface aquifers after spring melt.

The combination of volcanic gas addition and enhanced rock weathering will affect Icelandic river waters differently depending on their alkalinity; direct runoff rivers with low alkalinity will be more affected by eruption products than high alkalinity spring and glacier fed rivers due to their lower pH buffering capacity. Despite the significant chemical changes observed in the local rivers during and after the eruption, and in contrast to the chemical signals observed prior to subglacial floods, there was no substantial chemical composition signal in the local river water indicating the existence of the subglacial eruption prior to the Bárðarbunga eruption.

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Figures and Tables captions

Figure 1. Sampling locations. The 2014/15 Bárðarbunga eruption which produced the lava flow was formed on the historical Holuhraun lava field north of Dyngjujökull glacier as indicated in (a). The newly formed lava (Holuhraun lava as shown in b) extends towards NE and its surface indicates the fresh lava distribution on November 14, 2014, when the last sampling was performed. The triangles in (b) indicate water and the circles snow sampling locations. Black dot on the Icelandic map in (a) shows the location of the Fjarðará river.

Figure 2. The enrichment ratio of selected constitutes [mol/kg] in water samples collected downstream the lava flow (14−JF−6 and 14−JF−7) comparing to upstream sample 14−JF−5.

Figure 3. Dissolved major species concentrations versus discharge in samples collected at the Upptyppingar station before lava flowed into the main channel of the Jökulsá á Fjöllum on September 7, 2014.

Figure 4. Dissolved major species concentrations versus discharge in samples collected at the Upptyppingar station after lava flowed into the main channel of the Jökulsá á Fjöllum on September 7, 2014.

Figure 5. Discharge, water temperature, and element concentrations in waters collected by the osmotic sampler at the Grímsstaðir. Hot lava−water interaction caused the increase in dissolved SO_4 concentration while decreasing DIC, as indicated by the ellipse.

Figure 6. The dependence of the chemical composition of snow samples on pH which was calculated to the temperature of snow melting at 0.1 °C. Calculations were performed with the

PHREEQC computer code. Note that concentrations of Cd, Co, Cr, Cu, Ni, Pb, Zn, Ti, and V are presented only for snow samples A to I.

Figure 7. The dissolved carbon/SO_4 ratio in the Jökulsá á Fjöllum sampled at Upptyppingar, Grímsstaðir, the lava front (upstream and downstream from the lava) and in snow samples taken in vicinity of eruption site. The samples were collected at various stages of the Bárðarbunga unrest. The highest ratio carbon/SO_4 of 85 was measured in water collected in vicinity of the eruption site on October, 9, upstream from the lava and it is not included in this plot for better visualization. The conductivity shown in the figure was measured during spot sampling at Upptyppingar.

Figure 8. Measured conductivity plotted as a function of discharge in the Jökulsá a Fjöllum at Upptyppingar (a) and Grímsstaðir (b) during monitoring campaigns of 1983−2001 and during the 2014 Bárðarbunga unrest. Samples 'before' refer to water collected before the lava flowed into the main channel of the Jökulsá á Fjöllum, whereas samples 'after' correspond to conductivity in waters collected after lava flowed into the river channel.

Fig. 9. The aqueous species dominating the charge balance of melted snow samples in percent of charge contributed by each species for selected representative snow samples. Cations are illustrated on the left, anions on the right. Snow A represents the background snow. Snow D and H represent the most acidic snow, whereas sample J snow the most enriched in tephra.

Figure 10. Element ratios to Cl of melted snow samples collected in vicinity of the Bárðarbunga eruption site (2014) and in unpolluted snow samples collected at Langjökull glacier in 1997−2006. The seawater ratios were taken from Bruland (1983).

Figure 11. The dissolved fluxes of selected elements calculated at the Grímsstaðir monitoring station during the 1998−2001 (diamonds) and during the 2014 Bárðarbunga activity before (squares) and after (triangles) lava flowed into the Jökulsá channel.

Table1. Sample names, locations, sampling dates and times (GMT), GPS coordinates, discharge measured by IMO, water and air temperature, measured pH, and conductivity at the temperature given in the table (T [°C]/pH; T [°C]/Conductivity). The charge imbalance and *in situ* pH was calculated using the PHREEQC computer code at *in situ* temperatures (Parkhurst and Appelo, 1999). Water temperature values in bold were measured *in situ* with the portable probe. Other were taken from IMO continuous measurements.

Table 2. Concentration of dissolved constituents in water samples collected during this study. The charge imbalance and DIC concentration was calculated with the PHREEQC computer code (Parkhurst and Appelo, 1999). Values in italics were measured by ALS Sweden (see text). The IC and ICP−OES refer to the analytical technique (see Section 4.4).

Table 3. Samples names, description, sampling dates,and GPS coordinates of the snow samples collected in vicinity of the Bárðarbunga eruption site. The amount of snow melted, together with weight of sediments, pH and conductivity at temperature of measurements (T [°C]/pH; T

[°C]/Conductivity) and *in situ* pH is also presented. The *in situ* pH at 0.1 °C was calculated using the PHREEQC computer code at *in situ* temperatures (Parkhurst and Appelo, 1999).

Table 4. Concentration of dissolved constituents in melted snow samples collected during this study. The charge imbalance and DIC concentration was calculated with the PHREEQC computer code (Parkhurst and Appelo, 1999). The values in italics were obtained by ALS Sweden. The IC and ICP−OES refer to the analytical technique (see Section 4.4).