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PII:	S0009-2541(21)00271-0
DOI:	https://doi.org/10.1016/j.chemgeo.2021.120327
Reference:	CHEMGE 120327
To appear in:	Chemical Geology
Received date:	2 February 2021
Revised date:	30 April 2021
Accepted date:	15 May 2021

Please cite this article as: P. Delmelle, E.C. Maters, J.A. Calkins, et al., Eruptive style controls the formation of silicon hexafluoride salts on volcanic ash: The case of the 2010 eruption of Eyjafjallajökull volcano, Iceland, *Chemical Geology* (2021), https://doi.org/10.1016/j.chemgeo.2021.120327

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Eruptive style controls the formation of silicon hexafluoride salts on

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Iceland

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Revised manuscript submitted to Chemical Geology

30 April 2021

Abstract

The presence of fluoride (F)-bearing compounds in volcanic ash fallout is recognised to pose significant environmental and health hazards. Nevertheless, understanding of the formation and composition of these compounds remains limited, or even inconsistent. This hampers full comprehension of the risks and impacts elicited by fluorine-rich ash emissions after an explosive eruption. The 2010 activity of Eyjafjallajökull volcano in Iceland was characterised by contrasted eruptive styles - phreatomagmatic and magmatic - which produced ash deposits with distinct soluble F contents. Based on X-ray photoele tror spectroscopy and leachate analyses of Eyjafjallajökull ash materials, we infer the existence of silicon hexafluoride salts, particularly Na₂SiF₆, dominantly if not exclusively on the magmatic ash, and suggest a reaction mechanism for their formation. The presence of Na₂SiF₆ explains the much greater F⁻ concentration and higher acidity measured in leachates of the magmatic ash compared to those of the phreatomagmatic ash. River waters affected by ash deposition during the magmatic activity showed a temporary increase in F and decrease in dissolved silicon isotope values (δ^{30} Si). We contend that the formation of silicon hexafluoride salts on ash leads to a surface enrichment of the ash snicate glass and mineral components in ²⁸Si, with the release of this light Si from the nagmatic ash during the early stage of weathering causing a depression in the riverive δ^{30} Si. This supports existing evidence of silicate dissolution processes being influenced by the presence of F. Our study also points to the likely important role of Na₂SiF₆ in modulating the environmental and health effects of ash emissions from fluorine-rich magmatic eruptions.

Keywords: ash, Eyjafjallajökull volcano, fluoride, silicon hexafluoride salts, silicon isotopes

1. Introduction

Volcanic ash, the most widespread product of explosive eruptions, is often synonymous with environmental and societal disruptions. Among the sources of potentially detrimental effects, high concentrations of soluble fluoride (F') in fresh ash fallout are a cause for concern, as over-exposure to fluorine (F) may lead to negative health effects in humans and animals (Weinstein and Davison, 2004). There are numerous cases of acute and chronic F⁻ poisoning of grazing livestock following volcanic activity accompanied 'w ash and gas emissions (e.g., Roholm, 1934; Araya *et al.*, 1993; Shanks, 1997; Sigurdsson and Pálsson, 1957; Thordarson and Self, 2003). The deposition of ash in watersheds moy also alter the chemistry of surface waters (Frogner Kockum *et al.*, 2006). In particular the release of soluble F⁻ from ash may temporarily increase the riverine concentration of F⁻ and impact the aqueous speciation of aluminium (Al), and hence its toxicity, as reported after the 1991 and 2000 eruptions of Hekla volcano in Iceland (Flaathen and Gislason, 2007). Finally, the presence of dissolved F⁻ in water entering and percolating through the soil may significantly enhance silicate dissolution and possibly weathering rates (Wolft-Boenisch *et al.*, 2004).

While ash interaction with gives and condensates in the vertical eruption plume and laterallydispersed eruption clock is usually held responsible for deposition of F-bearing compounds on ash surfaces (Óskarsson, 1980; Delmelle *et al.*, 2007), precise information about their composition and the reaction pathways leading to their formation is patchy and uncertain. For example, Óskarsson (1980) concluded that at temperatures above 700 °C in the eruption plume, ash exposure to gaseous hydrogen fluoride ($HF_{(g)}$) favours calcium fluoride (CaF_2) deposits, whereas at lower temperatures below 600 °C a calcium silicon hexafluoride salt (CaSiF₆) predominates. Based on X-ray photoelectron spectroscopy (XPS) and transmission

electron microscopy (TEM) measurements of ash materials from Mt. Etna, Italy, Barone *et al.* (2016) suggested that the ash surface enrichment in halogens, including F, largely reflects sub(volcanic)surface processes occurring at the interface between gas bubbles and the silicate melt. They further attributed the rapid release of soluble F⁻ upon leaching of the ash to the dissolution of physisorbed HF. Recently, Bia *et al.* (2020) applied XPS to examine ash samples from different volcanoes in the southern Andes and claimed that sodium fluoride (NaF), CaF₂ and/or apatite (Ca₅(PO₄)₃(OH, Cl, F)) are the main soluble F-containing compounds on the ash surfaces.

An improved description of the mechanism(s) responsible for the formation of soluble Fbearing compounds on ash would contribute to increasing our capacity to anticipate the health and environmental hazards posed by explosive any ptions involving F-rich emissions. In this regard, a rare opportunity was presented the dree 39-day long 2010 eruption of the glaciercapped Eyjafjallajökull volcano, Iceland, which began with phreatomagmatic activity before abruptly switching to purely magmatic episodes (Gudmundsson *et al.*, 2012). As initially recognised by Gislason *et al.* (2^{t} 11), the two types of activity produced contrasted in-plume physical and chemical conditions for gas/condensate-ash interactions. Here, we combine XPS and ash leachate meas irenents to investigate factors that influence the formation and composition of soluble F- earing deposits on ash surfaces. We also analysed the chemical and Si isotopic compositions of two river catchments in the vicinity of Eyjafjallajökull volcano at three different periods in 2010, to assess whether ash materials from the phreatomagmatic and magmatic eruptions affected the chemistry of local surface waters. The rationale for measuring dissolved Si isotopes in the river samples stems from experimental observations during basalt dissolution, here possibly enhanced at ash surfaces by dissolved F, of Si isotopic fractionation between solid and dissolved phases (Ziegler *et al.*, 2005; Chemtob *et al.*, 2015).

2. Materials and Methods

2.1 Ash samples

The April to May 2010 summit eruption of Eyjafjallajökull volcano is divided into three distinct ash-producing phases; an early phreatomagmatic phase designated *P-II*, followed by magmatic phases designated *P-II* and *P-III* (Gudmundsson *et al.*, 2012). Two ash samples from each of the three eruptive phases (EYJ-A19 and EYJ-A40 for *P-I*, EYJ-A8 and EYJ-A14 for *P-II*, and EYJ-A26 and EYJ-A30 for *P-III*) were studied in detail (Table 1). The six ash samples were collected at various distances within approximately 38 km downwind of the volcano summit (Fig. 1). They correspond to fresh material that did not come in contact with water, snow or the soil surface upon deposition and atte wards. Additional details on the three eruptive phases and the ash sampling are provided in the Supplementary Information (SI).

Insert Figure 1 here

Insert Table 1 here

2.2 Ash bulk composition and mineralogy

The bulk composition of the six ash samples from *P-I*, *P-II* and *P-III* was determined on the crushed material by in⁴...ctively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Fisher Scientific iCAP 6500) after alkaline fusion at 1000 °C with a 1:4 $Li_2B_4O_7$:LiBO₂ mixture (Chao and Sanzolone, 1992). The total content of F in the ash was obtained by mixing a sub-sample of the crushed ash with LiBO₂. After sintering at 1050 °C, the sintrate was dissolved in concentrated HNO₃, and the F concentration in solution was measured with an ion-selective electrode (Orion Research, Model 920) after addition of a total

ionic strength adjustment buffer (Bodkin, 1977). This method was tested successfully on the US Geological Survey reference basaltic rock material BHVO-2, for which a total F concentration of 370 mg kg⁻¹ is reported (Wilson, 1997) and a concentration of 366 ± 58 mg kg⁻¹ (n = 4) was measured. The bulk mineralogy of the ash was obtained by X-ray powder diffraction (XRD; Bruker D8 Advance) using a monochromatic Cu_{Ka} X-ray beam and operating at 40 kV and 30 mA, a 0.02° step width and a 2.0 s step⁻¹ counting time. The X-ray diffractograms were analysed with the EVA[©] software. The detection limit for minerals in the ash is 5 wt.%.

2.3 Ash surface composition and specific surface area

The surface (~2-10 nm depth) composition of the sL ash samples was measured by XPS (Kratos Axis Ultra) using a monochromatic Al_{k} X-ray beam centred at 1486.6 eV and slow electron charge compensation. The irrar atel sample surface area was ~700 µm x 300 µm. Survey spectra were recorded with c pass energy of 160 eV and a step of 1 eV. High resolution spectra of the C_{1s}, O_{1s}, Si _v. Al_{2p}, Fe_{2p}, Mg_{2p}, Ca_{2p}, Na_{1s}, K_{2p}, Cl_{2p}, S_{2p} and F_{1s} photopeaks were acquired with a pass energy of 40 eV and a step of 0.1 eV. The binding energy scale was calibrated by assigning a value of 284.8 eV to the C_{1s} photopeak for adventitious C. The X₁S s_p-ctra were processed using the CasaXPS[©] software.

The specific surface area (a_s) of the ash samples was obtained, after overnight degassing at 150 °C, from a five-point Kr_(g) adsorption isotherm at -196 °C (Micromeritics ASAP 2000) based on the Brunauer, Emmet and Teller model (Brunauer *et al.*, 1938).

2.4 Ash leachate composition

In addition to the six ash materials described above, 14 ash samples from the *P-I*, *P-II* and *P-III* eruptions were collected in the same areas as the other specimens and analysed for their soluble element concentrations. The ash leachates were obtained by gently shaking the ash with ultrapure water at a ratio of 1:100 (g ash to ml water) for 45 minutes, and subsequently centrifuging at 5000 rpm to separate the leached solution from the ash material. A sub-sample of the leachate was used for pH measurement and the remainder was filtered through a 0.2 µm cellulose acetate membrane filter. Dissolved F⁺, Cl⁺ and SO₄²⁻ were measured by ion chromatography (IC; Dionex ICS-2000, equipped with an IonPoct⁺⁺ AS15 column) and Si, Al, Fe, Mg, Ca, Na, K and P by ICP-AES. The precision for the conton and cation determinations is better than 5%. The saturation of the leachates with respect to various solid phases, including those bearing F (e.g., metal fluoride and si⁺icc⁺⁺ hexafluoride salts), was tested with the PHREEQC geochemical modelling program (Parkhurst and Appelo, 1999).

2.5 River water pH and dissolved element concentrations

Two river catchments in southern Ice at d were sampled to assess the potential effects of the Eyjafjallajökull eruption on the consposition of local surface waters. Specifically, water from the Markarfljót and Jökulsa \leq Scheimasandi glacial rivers (Fig. 1) was collected on 24 April, 8 May and 5 August 2010, i.e. several days after *P-I*, during *P-III*, and nearly three months after the eruptions ended, respectively. These rivers' drainage basins were variably exposed to ash fall during the eruptions. The sampling site at Jökulsá \leq Sóheimasandi river was directly under the *P-III* ash plume (Fig. S1). The pH was measured in the field prior to filtration of the water samples through a 0.2 µm cellulose acetate membrane filter. The concentrations of F⁻, CI⁻ and SO₄²⁻ and Si, Al, Fe, Mg, Ca, Na and K were determined by IC and ICP-AES, respectively.

2.6 River water silicon isotopic composition

Sub-samples of the river water, filtered and acidified with HNO₃ to pH ~2 in the field, were prepared for Si isotopic analysis according to Georg *et al.* (2006). The Si isotope composition was determined on a Nu Plasma High Resolution-Multi Collector ICP Mass Spectrometer in dry plasma mode using a Cetac Aridus II desolvating system. The measurements were carried out following the protocol detailed in Opfergelt *et al.* (2013). The Si isotope composition is expressed as δ^{30} Si, defined as the deviation in per mil (‰) of the isotope ratio of the sample relative to that of the standard reference material NBS-?8 : ilica sand, where δ^{30} Si = [(30 Si/ 28 Si)_{sample}/(30 Si/ 28 Si)_{standard} -1] x 1000.

3. Results

3.1 Ash bulk composition and mineralogy

The bulk composition, including total F content, of the six ash specimens from *P-I*, *P-II* and *P-III* is reported in Table S1. The samples all conform to a benmoreitic to trachytic composition, in accordance with previous studies (Sigmarsson *et al.*, 2011; Horwell *et al.*, 2013). The total F content in the ash varies between 843 and 1297 mg kg⁻¹, with the highest total F content occurring in the *P-II* ash.

The XRD analysis did not reveal the presence of crystalline F-bearing minerals in any of the six ash materials. We note that Sigmarsson *et al.* (2011) reported fluorite (CaF₂) in their microprobe analyses of microsyenitic fragments in ash erupted on 17 April 2010 (i.e. *P-I*). This mineral was not detected in our samples by XRD and therefore, if present, its content must be <5 wt.%.

3.2 Ash surface composition and specific surface area

The surface composition (elements for which the concentrations were above the 0.1 at.% detection limit) of EYJ-A19 and EYJ-A40 (*P-I*), EYJ-A8 and EYJ-A14 (*P-II*), and EYJ-A26 and EYJ-A30 (*P-III*) before and after leaching with ultrapure water is shown in Figure 2 and reported in Table S2. The *P-II* and *P-III* ash exhibit much higher surface F concentrations (up to 12.0 at.%) than the *P-I* ash (<0.4 at.%). Such marked differences are not observed for surface Cl concentrations across the phreatomagmatic and mematic ash, with Cl occurring only on EYJ-A19, EYJ-A8 and EYJ-A26 in low concent atic is (0.3, 0.6 and 0.2 at.%, respectively). Sulphur is not detected on any of the *est* sa nples. The XPS analysis also reveals that the surface F concentrations are strong y is duced (by 89-94%) and below the detection limit on the leached *P-II* and *P-III* and *P-III* ash the surfaces. Magnesium occurs on the *P-I* ash but is not detected on three of the four magmatic ash samples. The surface S and the surfaces of alkali and alkaline earth metals are variably affected by leaching.

Insert Figure 2 here

The *P-I* ash specimens have significantly larger a_s (3.5 and 7.5 m² g⁻¹) than the magmatic *P-II* and *P-III* ash materials (0.2 m² g⁻¹) (Table S3). This conforms with previous results (Gislason *et al.*, 2011; Paque *et al.*, 2016).

3.3 Ash leachate composition

The concentrations of F, Cl, SO_4^{2-} , Mg, Ca, Na and K in the *P-I* (EYJ-A19 and EYJ-A40), *P-II* (EYJ-A8 and EYJ-A14) and *P-III* (EYJ-A26 and EYJ-A30) ash leachates are illustrated

in Figure 3. Table S3 reports the leachate compositions of the 20 ash samples. The percent charge-balance error for 14 of the 20 samples analysed is $\leq 20\%$; it varies between 22 and 29% for the others. None of the leachate solutions are saturated with respect to a F-bearing mineral phase, i.e. CaF₂, Ca₅(PO₄)₃F, NaF, AlF₃, Na₂SiF₆, K₂SiF₆ or CaSiF₆.

Insert Figure 3 here

The *P-I* ash leachates have pH values ranging from 7.3 to 7.9, whereas leachates of the magmatic ash are consistently acidic with pH values between 3.7 and 5.9. Sodium is the main cation in all leachates. The concentration of soluble F^- varies broadly (~1-63 µmol g⁻¹ ash) but is systematically and significantly higher in the magmatic ash than in the phreatomagmatic ash; with F^- being the dominant ion by far in the form r samples. Among all ash leachates, those of the *P-II* ash are most acidic (pH 3.7-4. Y at d richest in F^- (29-63 µmol g⁻¹ ash). Our ash leachate compositions for the *P-II* and *P-III* ash are in general agreement with those reported by Gislason *et al.* (2011) and Bagnato *et al.* (2013). These authors did not examine ash material from the eruption phase *I -1*.

3.4 River water pH and disso."vei clement concentrations

The composition of the Mr rkarfljót and Jökulsá á Sólheimasandi river water samples is shown in Table S4. The percent charge-balance error is $\leq 12\%$ for the analyses, except for the Markarfljót river sampled on 8 May 2010, which has an excess cation charge of ~30%. The river waters are undersaturated with respect to F-bearing mineral phases and have near-neutral to alkaline pH values (6.9-7.9). Across the three river sampling dates in 2010, dissolved F⁻ concentrations differ markedly (Fig. 4). For both rivers, the lowest concentrations (0.02 and 0.01 mmol l⁻¹) are recorded in August, whereas F⁻ is higher by about ten times in April (0.23 mmol l^{-1}) and forty times in May (0.43 mmol l^{-1}) in the Markarfljót and Jökulsá á Sólheimasandi waters, respectively. The other major dissolved elements do not show such large variations.

3.5 River water silicon isotopic composition

The Si isotope composition of dissolved Si in the Markarfljót river water samples varies between $\pm 0.70 \pm 0.05$ and $\pm 0.93 \pm 0.12\%$ (Table S4). While the δ^{30} Si of the Jökulsá á Sólheimasandi river water in April is comparable, much lower values are found in May (-0.27 $\pm 0.16\%$) and August ($\pm 0.40 \pm 0.11\%$) (Fig. 5).

Insert Figure 4 here

4. Discussion

4.1 Variations in F concentration of the P.1, P-II and P-III ash

The total F content of the *P-I*, *P-I* \in In ¹ *P-III* ash compares well with the range of values (1013-1171 mg kg⁻¹) reported for representative Icelandic rocks of basaltic andesite, andesite and dacite compositions (Stech, *, 1998). However, unlike the bulk F, the concentration of F in the ash surface varies sign ficantly across the *P-I*, *P-II* and *P-III* ash specimens (Fig. 2 and Table S2). The surface i the *P-II* and *P-III* ash materials contains 39-40 and 11-12 times more F, respectively, than the surface of the *P-I* ash EYJ-A19 (no F was detected on EYJ-A40). Gislason *et al.* (2011) highlighted a similar difference between the surface composition of two ash samples from the *P-I* and *P-III* eruptions. The much higher concentration of F on the *P-III* and *P-III* ash reflects a strong enrichment at the surface relative to the bulk. However, exposure to ultrapure water annihilates this feature, indicating that the surplus of F on the *P-II*.

and *P-III* ash surfaces originates from soluble F-bearing compounds. Convincingly, the *P-II* and *P-III* ash leachates contain much more F^- (~31 and ~15 times on average, respectively) than the *P-I* ash leachates (Table S3). We emphasise that a grain size effect cannot account for this result; normalising the leachate composition to the ash's specific surface area (data available for EYJ-A19, EYJ-A40, EYJ-A8, EYJ-A14, EYJ-A26 and EYJ-A30) exacerbates the large difference in soluble F^- concentrations between the phreatomagmatic and magmatic samples, i.e. a consequence of the higher a_s of the *P-I* ash (3.5 and 7.5 m² g⁻¹) compared to that of the *P-II* and *P-III* ash (all 0.2 m² g⁻¹; Table S3).

While primary magmatic minerals such as CaF_2 and $Ca(PO_4)_3F$ (Piccoli and Candela, 2002; Scaillet and Macdonald, 2004) in ash may be a source of soluble F, the large F⁻ concentration found in some ash leachates is believed to originate primarily from the dissolution of readily soluble compounds formed by reactions brive n ash particles and gases and condensates coexisting in the eruption plume and cloud (e.g., Óskarsson, 1980; Armienta et al., 2002; Delmelle et al., 2007; Bagnato et al., 2015). In a limited number of ash leachates, Borisova et al. (2012) attributed a trend of decreasing CI:F and increasing CI:S ratios to progressive degassing of a trachyandesitic magma, with preference for volatile exsolution following the order $SO_2 \approx H_2S \ge Cl \gg F$ (e.g., Carroll and Webster, 1994), as the eruptive activity evolved from phreatomagmatic to magmatic. Information on magmatic volatile composition during the Eyjafjallajökull eruption is scarce, and caution is needed in inferring such compositions directly from ash leachates, due to differential partitioning of SO_{2(g)}, HCl_(g) and HF_(g) into condensates and/or onto ash in the eruption plume and cloud (Martin et al., 2012). Gislason et al. (2011) suggested that the comparatively low content of soluble F^- on the *P-I* ash relates to preferential partitioning of volatiles including HF_(g) into liquid water during the initial phreatomagmatic eruptive activity at Eyjafjallajökull. While the Cl:S ratios obtained for our

extended leachate dataset lie within a relatively narrow range (1.13-5.18) across all phreatomagmatic and magmatic ash leachates, significant removal of $HF_{(g)}$ by liquid water during *P-I* is consistent with the dramatically lower CI:F ratios (~23 and ~12 times on average for *P-II* and *P-III*, respectively) in the magmatic ash leachates (Table S3 and Fig. 5). In contrast to $SO_{2(g)}$ and $HCl_{(g)}$, $HF_{(g)}$ is fully miscible (dissolves without limit) in water (National Center for Biotechnology Information, 2021).

Insert Figure 5 here

Gudmundsson et al. (2012) and Magnússon et al. (2012) showed that the first phase of the eruption was characterised by discharge of magmatic gases and fragments through ice cauldrons formed over the summit vent of the gia er-capped Eyjafjallajökull volcano. Additionally, Cioni et al. (2014) inferred that a significant proportion of the fragmented material fell back into the ice/meltwater filled vent before being expelled again by explosive eruption. Effective scrubbing of wate, soluble magmatic gases, notably HF_(g), likely limited its availability for interaction with as n in the early eruption plumes/clouds. The elevated F concentration measured on 2 A_Fril in the Markarfljót river, into which meltwater was discharged during P-I of the eruption, conforms to this hypothesis (see section 4.4). Moreover, syn-eruptive leaching of the ash material likely took place in the ice/meltwaterfilled vent, thereby removing any salts that had formed on the ash surfaces. However, these conditions did not persist, as a tephra cone that had built up within the active vent at the end of *P-I* effectively isolated the rising magmatic gas-ash mixture from ice/meltwater. Thus, the "drier" eruptive conditions of the magmatic activity that ensued probably allowed more efficient interaction between HF_(g) and ash in the eruption plumes/clouds, in turn accounting for the large soluble F⁻ enrichments measured on the *P-II* and *P-III* ash materials.

4.2 Nature of F-bearing compounds on the P-I, P-II and P-III ash

Effective removal of F from the surfaces of the ash samples after exposure to water (Table S2, Fig. 2), which produced the high F⁻ concentrations in the *P-II* and *P-III* ash leachates (Table S3), confirms that F on the ash surfaces occurs largely in soluble form. The results of speciation calculations performed with PHREEQC also indicate that all the ash leachates are undersaturated with respect to various F-bearing minerals and thus, dissolved F is not controlled by mineral solubility. To test if the P-I, P-II and P UI ash materials contain other less soluble F-bearing compounds, we also measured the dissolved F⁻ concentration in solutions obtained by extracting a subset of samples with 0.01 mol l^{-1} HCl (using the same protocol as that described for the water leaching). As revealed in Figure S2, acidic leaching of the P-I ash resulted in ~4 to 6 times higher F^- concentrations than in the water leachates. In contrast, extracting the magmatic ash specime... with HCl did not lead to such compositional changes, i.e. the dissolved F⁻ concentrations parallel those found in the water leachates. These results indicate the occurrence of F in poorly water-soluble forms in the *P-I* ash, and confirm the high solubility of the F-be ring compounds on the P-II and P-III ash surfaces. As mentioned earlier, minor Car was identified in the pyroclasts ejected during P-I of the eruption (Sigmarsson *et il.*, 2011). The solubility of CaF₂ in water is low (i.e. 2.0×10^{-4} mol l⁻ ¹ or 1.6 x 10⁻² g l⁻¹ at 25 °C; Haynes et al., 2017) but increases at acidic pH values, in accordance with our observations for the P-I ash.

While many ash leachate studies have long highlighted the presence of water-soluble Fbearing compounds on ash surfaces (e.g., Thorarinsson, 1979; Óskarsson, 1980; Cronin *et al.*, 2003; Delmelle *et al.*, 2007; Armienta *et al.*, 2011; Bagnato *et al.*, 2011; Gislason *et al.*, 2011; Olsson *et al.*, 2013; Bia *et al.*, 2020), their nature remains enigmatic; they have not been

observed directly in natural samples and ash leachate compositions cannot be reconciled with the dissolution of simple fluoride salts.

Nevertheless, several authors have suggested various compositions for representing the Fbearing compounds from which soluble F in ash originates. For example, Cronin *et al.* (2003) examined the ash from the 1995-1996 eruption of Mt. Ruapehu, New Zealand, and posited that soluble F-bearing deposits (such as CaSiF₆ and NaF) were primarily associated with material from purely magmatic explosive events, whereas comparatively less soluble phases (such as CaF₂, MgF₂ and Ca₅(PO₄)₃F) dominated in ash from eruptions involving the disruption of a magmatic hydrothermal system. More represently, using TEM, Barone *et al.* (2016) found discrete aggregates containing F, S, Cs and Mg on the surfaces of ash particles from the 2013 eruption of Mt. Etna, Italy. Also $\frac{1}{2}$, sed on XPS and TEM analyses, Bia *et al.* (2020) inferred the presence of F in particles achering to the surfaces of ash emitted by recent eruptions of Chilean volcanoes, and specula. d that the F-bearing compounds corresponded to CaF₂ and Ca₅(PO₄)₃(OH, Cl, F) "pre apirated as thin coatings onto the glass particles".

In a previous study, Gislason *e at.* (2011) applied inverse geochemical modelling to interpret the leachate chemistry of the *P*-*I* and *P*-*III* ash from the 2010 Eyjafjallajökull eruption. The authors argued that $NaMe_{A}M$

The XPS F_{1s} spectra obtained for the *P-I*, *P-II* and *P-III* ash can be described by a peak centred at 685.3 eV with a full width at half maximum of 2 eV, possibly reflecting composite contributions from various F-bearing compounds such as FeF₂, FeF₃, CaF₂, MgF₂, CaSiF₆, Na₂SiF₆ and K₂SiF₆ (Hess *et al.*, 1994). Alternatively, F in Al-F or Si-F bonds at silicate glass surfaces could also account for the F_{1s} peak shape (Deshkovskaya and Shschukarev, 2013). The low conductivity of the ash material, resulting in varying sample charging and shifts of the F_{1s} peak towards higher binding energies, precludes a reliable peak-fitting process and thus, a chemically meaningful description of the different components contributing to the peak envelope.

While the XPS analyses cannot confirm the presence of silicon hexafluoride salts on the surfaces of the *P-II* and *P-III* ash specimens, the leachate compositions provide additional insights. Sodium is the most abundant option, in all ash leachates, possibly pointing to a dominant role for a Na-containing salt (Fig. 3). The Na:F molar ratio in the *P-I* ash leachate varies between ~8.5 and 20.3, where a much lower values are found for *P-II* and *P-III* ash leachates, i.e. ~0.2 to 0.5 (Table §3). The dissolution of Na₂SiF₆ will produce a Na:F ratio of ~0.33, in good agreement with the leachate composition obtained for the magmatic ash. In contrast, the large excess of the phreatomagmatic ash. The elemental ratios in the leachates are incompatible with the dominant occurrence of other types of silicon hexafluoride salts, i.e. K₂SiF₆ and CaSiF₆. Alkali and alkaline earth metals in the ash leachates could also originate from the dissolution of chloride and sulphate salts, typically NaCl and CaSO₄, formed primarily by reactions between magmatic gases and ash particles in the hot core of the eruption plume (Witham *et al.*, 2005; Ayris *et al.*, 2013; Ayris *et al.*, 2014). However, the Na:Cl ratio in all ash leachates but one is >1 (Fig. S3), implying that the dissolution of NaCl

deposits alone cannot explain the leachate compositions for either the *P-I*, *P-II* or *P-III* ash. Similarly, the presence of $CaSO_4$ as a major deposit on the ash surfaces is not supported by the leachate compositions (Fig. S3)

Sodium silicon hexafluoride has a high solubility, i.e. on the order of $3.5-4.0 \times 10^{-2} \text{ mol I}^{-1}$ at 25 °C (or 6.7-7.6 g I⁻¹; Haynes *et al.*, 2017; Spellman, 2020). This is consistent with the elevated F concentration measured in the *P-II* and *P-III* ash leachates (Table S3). The dissolution of Na₂SiF₆ in water also generates acidic solutions (Rees and Hudleston, 1936; Crosby, 1969). Using PHREEQC, it can easily be shown that the dissolution of Na₂SiF₆ (or any other silicon hexafluoride salt of alkali or alkaline earch metal) produces acidic pH values <3.5. The overall dissolution-hydrolysis reaction for the silicon hexafluoride is (Rees and Hudleston, 1936; Crosby, 1969; Urbansky and Scheck, 2000; Urbansky, 2002):

$$Na_2SiF_{6(s)} \rightleftharpoons 2Na^+_{(aq)} + SiF_{6(aq)}^{2-}$$
[1a]

followed by:

$$SiF_{6}^{2-}{}_{(aq)} + 4 H_2 O_{(l)} \rightleftharpoons H_4 Si' {}_{(aq)} + 4 HF_{(aq)} + 2 F^{-}{}_{(aq)}$$
[1b]

In the case of a phrea om gmatic eruption, ash leachate acidity relates to oxidation of elemental sulphur and/or pyrite (FeS_2) eroded from the volcanic conduit and incorporated into the ash material (e.g., Le Guern *et al.*, 1980; Cronin *et al.*, 1998). For purely magmatic explosive events, the presence of H₂SO₄ and HCl droplets on the surface of ash is often invoked to explain the low pH values of some leachates (Witham *et al.*, 2005 and references therein). In our opinion, this theory is incorrect because once in contact with the ash's silicate glass and minerals, such strong aqueous acids will be neutralised through rapid metal for

proton exchange reactions (e.g., Oelkers and Gislason, 2001; Oelkers 2001). As a result, H_2SO_4 and HCl cannot exist freely on ash surfaces.

It is in fact the nature of the salts existing on the surface of ash that dictates if a leachate will acquire acidity. The salts that form dominantly through gas/condensate-ash reactions at high temperatures in the eruption plume and perhaps also in the cooler eruption cloud are NaCl and CaSO₄ (Hinkley and Smith, 1982; Witham *et al.*, 2005; Bagnato *et al.*, 2011; Ayris and Delmelle, 2012), but both will generate a neutral pH wher dissolved in pure water. At Eyjafjallajökull, we argue that the presence of silicon hexafluorid, salts is required to account for the acidity of the *P-II* and *P-III* ash leachates. We further surmise that these F-bearing salts are similarly responsible for the acidic pH v due: sometimes reported for leachates derived from purely magmatic ash. Convincing¹_y, the ash from the 2000 magmatic eruption of Hekla, Iceland, produced an acidic leachate (τ H = 3.4) with a high F⁻ concentration when exposed to deionised water (Frogner et al., 2^{\cent}01). Low pH values (<3) are also inferred based on the F-rich leachate compositions are crubed by Óskarsson (1980) for the Hekla ash emitted during the Plinian phase of the 1^c70 c-uption.

4.3 Formation of silicon hearfl wride salts on the P-II and P-III ash

The presence of F-bearin, compounds, including silicon hexafluoride salts, on the surface of ash may be the result of various reactions. At high temperatures (>600 °C), metal-bearing silicates may react with $HF_{(g)}$ to produce the simple metal fluoride salts suggested by others (e.g., Cronin *et al.*, 2003; Barone *et al.*, 2016; Bia *et al.*, 2020) to exist on ash originating from F-rich eruptions, as well as the volatile compound silicon tetrafluoride (SiF_{4(g)}):

$$Al_2SiO_{5(s)} + 10 HF_{(g)} \rightarrow 2 AlF_{3(s)} + SiF_{4(g)} + 5 H_2O_{(g)}$$
 [2]

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$$CaSiO_{3(s)} + 6 HF_{(g)} \rightarrow CaF_{2(s)} + SiF_{4(g)} + 3 H_2O_{(g)}$$
 [3]

$$Mg_2SiO_{4(s)} + 8 HF_{(g)} \rightarrow 2 MgF_{2(s)} + SiF_{4(g)} + 4 H_2O_{(g)}$$
 [4]

$$Fe_2SiO_{4(s)} + 10 HF_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow 2 FeF_{3(s)} + SiF_{4(g)} + 5 H_2O_{(g)}$$
 [5]

These reactions were proposed by White and Hochella (1992) to explain surface element enrichment and depletion patterns on a Kilauea basalt lava flow, Hawai'i, hypothetically accompanying $HF_{(g)}$ degassing at the cooling lava surface. The simple metal fluoride salts were not identified on the lava but inferred from XPS element rates approximately matching their stoichiometries. Analogous reactions might have occurred during interaction of ash and $HF_{(g)}$ in the hot core of the Eyjafjallajökull eruption pluces. However, the time window for such reactions >600 °C was probably short during the moderately-sized eruptions (VEI 3; Gudmundsson *et al.*, 2012).

Silicon hexafluoride salts such as Na₂S. F_{5} , K₂SiF₆ and KNaSiF₆ (heklaite) have been identified in fumarolic incrustations in Iceland and are thought to be a product of water/gasrock interaction (Jacobsson *et a*¹, 20.98; Garavelli et al., 2010). By analogy, we suggest that reactions other than those described by equations [2-5] can occur at lower temperatures in the cooling eruption plume /clcuds. These involve aqueous HF and are responsible for the emplacement of silicon h xafluoride salts on the *P-II* and *P-III* ash surfaces. Insight on these reactions is provided by a large body of literature from the glass and microelectronics industries, which have widely made use of HF for etching of pure silica (SiO_{2(s)}) or multicomponent glasses in the vapour or aqueous phase (e.g., Holmes and Snell, 1966; Spierings, 1993; Monk *et al.*, 1993). Hydrofluoric acid is a weak acid ($pK_a = 3.17$; Harris, 2015) in H₂O₍₁₎, and its dilute aqueous solutions typically contain HF, H⁺, F, HF₂⁻, and H₂F₂ in equilibria (Warren, 1971; Spierings, 1993).

According to Knotter (2000), the first step in reaction of $SiO_{2(s)}$ and $HF_{(aq)}$ is protonation of surface silanol groups (\equiv Si-O⁻, \equiv Si-OH, or \equiv Si-OH₂⁺, depending on pH), followed by elimination of the OH⁻ or H₂O to form a \equiv Si⁺ intermediate. This intermediate reacts with HF₂⁻ (aq) or H₂F_{2(aq)} to produce \equiv Si-F by nucleophilic addition of F⁻. Subsequently, \equiv Si-F is broken from the SiO_{2(s)} network by three rapid nucleophilic substitution reactions of F⁻ on \equiv Si-F as H⁺ cleaves the bridging Si-O bonds, ultimately releasing SiF_{4(g)}. The overall reaction is summarised by:

$$SiO_{2(s)} + 4 HF_{(aq)} \rightarrow SiF_{4(g)} + 2 H_2O_{(l)}$$
 [6]

Silicon tetrafluoride can react further with $HF_{(-1)}$ and/or $H_2O_{(1)}$ to produce the non-volatile fluorosilicic acid ($H_2SiF_{6(aq)}$) (Jacobson, 1922 ··· 1923b; Piret *et al.*, 2018), which is a strong acid similar to H_2SO_4 and will dissociate in water (Urbansky, 2002). The corresponding reactions are:

$$SiF_{4(g)} + 2 HF_{(aq)} \rightarrow H_2 SiF_{\epsilon'aq)}$$
[7]

$$3\,SiF_{4(g)} + 4\,H_2O_{(l)} \rightleftharpoons 2\,\kappa_2Si_{6(aq)} + H_4SiO_{4(aq)}$$
[8]

$$H_2 SiF_{6(aq)} \rightarrow 2 H^+_{(aq)} + 2 SiF_6^{2-}_{(aq)}$$
[9]

Fluorosilicic acid similarly forms on the surface of multicomponent silicates, as shown by Yao and He (2013) for a commercial multioxide glass (72.5 wt.% SiO₂) exposed to a vapourphase mixture of HF, SiF₄ and H₂O. In the case of such silicates, metal cations in the SiO₂ network reduce the proportion of Si atoms bonded to four bridging O atoms, so enhancing the dissolution rate compared to pure SiO_{2(s)} (Spierings, 1991, Knotter, 2000; Oelkers, 2001).

Prior to dissolution, rapid exchange of alkali and alkaline earth metal cations (e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺) from the silicate with $H^{+}_{(aq)}$ from solution produces a hydrated SiO₂-rich surface layer (Spierings, 1991; Oelkers and Gislason 2001; Oelkers 2001), which is then broken apart by the actions of $H^{+}_{(aq)}$, $H_2F_{2(aq)}$, and $HF_2^{-}_{(aq)}$, as described above. The co-presence of strong acids such as $HCl_{(aq)}$ accelerates breakdown of the silicate network by supplying additional H^{+} to facilitate Si-O (and Al-O) bond cleavage (Li *et al.*, 2016).

By analogy, upon condensation of the magmatic gas mixture including $H_2O_{(g)}$, $SO_{2(g)}$, $HCl_{(g)}$ and $HF_{(g)}$ in the cooling Eyjafjallajökull eruption plumes clouds, the *P-II* and *P-III* ash surfaces likely developed an aqueous film and/or become immersed in acidic droplets containing variable quantities of dissolved fluorine species (HF, H_2F_2 , H^+ , F^- , HF^{2-} , SiF_6^{2-}), H_4SiO_4 and various cations, including alkali and alkaline earth metals. Presumably, silicon hexafluoride salts of alkali and alkaline salth metals formed on these ash surfaces by precipitation according to:

$$2 M_{(aq)}^{+} + SiF_{6(aq)}^{2-} \rightleftharpoons M_2 SiF_{6(c)}$$

$$[10]$$

$$M^{2+}_{(aq)} + SiF_{6}^{2-}_{(aq)} \rightleftharpoons MSiF_{6}_{(c)}$$
[11]

where M is an alkali [10] on Mkaline earth [11] metal cation (Piret et al., 2018).

Broadly consistent with the temperature-dependent sets of reactions between ash and HF proposed above, in laboratory experiments on Hekla ash exposed to boiling HF-H₂O vapours, Óskarsson (1980) suggested that CaF_{2(s)} formed >700 °C whereas CaSiF_{6(s)} formed at lower temperatures (down to 150 °C). Detection of Ca salts in particular by Óskarsson (1980), and not salts of other metal cations, may reflect a relatively higher mobility of Ca at the surface of this ash material, which had already been exposed to high temperatures in the Hekla 1970

eruption plume prior to the experiments. This would be consistent with Ayris et al. (2014) who inferred that surface oxidation of Fe(II) to Fe(III) above the glass transition temperature is accompanied by an increased incorporation of Na in charge-compensating positions, thereby lowering its mobility while permitting a greater outward diffusion of Ca.

4.4 Differential impact of the P-I and P-III ash on river chemistry

The highest F⁻ concentration in the Markarfljót river was detected on 24 April, several days after P-I of the eruption, but is not mirrored in the convosition of the Jökulsá á Sólheimasandi river sampled on the same date (Fig. 4). During P-I, both river catchments were exposed to ash fallout (Gudmundsson et al., 2012), implying that the P-I ash was not a major source of soluble F, consistent with our XPS and 'eachate findings. Instead, the high F concentration in the Markarfljót river on 24 A₁ r.1 is attributed to meltwater discharges into this river during P-I (Thorkelsson, 2012). The meltwater was likely enriched in volatiles, including F, degassed from the subgracial lava flow. Neither river received ash input during P-II of the eruption, which produced minor ash emissions (Gudmundsson et al., 2012). Remarkably, F concentrations in de Jökulsá á Sólheimasandi water increased six-fold from 24 April (shortly after *P-I*) a May (during *P-III*). This can be explained by dispersal of the soluble F-rich P-III asi to the south and southeast (Gudmundsson et al., 2012), affecting the Jökulsá á Sólheimasandi catchment (Fig. 1) but not the Markarfljót river. This is fully supported by a sharp increase in conductivity of the former river recorded on 5 to 8 May by the Iceland Meteorological Office, testifying to substantial inputs of ions dissolved from the fresh ash fallout (Thorkelsson, 2012).

The Si isotope composition of the Markarfljót river water across the three sampling dates falls within a relatively narrow range of δ^{30} Si values, i.e. +0.70 ± 0.05 to +0.93 ± 0.12‰,

conforming to values reported for other Icelandic glacial rivers (Georg *et al.*, 2007). While a similar isotopic signature is obtained for the Jökulsá á Sólheimasandi river water collected on 24 April, much lighter isotopic compositions are recorded for the May and August samples, i.e. δ^{30} Si = -0.27 ± 0.16 and +0.40 ± 0.11 ‰, respectively, pointing to a peculiar behaviour of the *P-III* ash deposited to this catchment during the later period of Eyjafjallajökull eruptive activity.

Although the δ^{30} Si of the Jökulsá á Sólheimasandi river on 3 May approaches the typical signature of an Icelandic basalt, i.e. δ^{30} Si = -0.35‰ (Sava e *e. al.*, 2011), if this isotopic signature were paralleled in the *P-III* erupted ash, total discolution of the ash deposited in the river catchment would be required to explain the and manously low δ^{30} Si value on 8 May. As total dissolution did not occur, we instead argue that the atypical Si isotopic composition of the 8 May Jökulsá á Sólheimasandi river water relates to dissolution of *P-III* ash with a strongly ³⁰Si-depleted surface, generated by volatilisation of Si in the form of SiF_{4(g)} during ash-HF_(g/aq) interaction in the eruption brune/cloud (reactions [2-6]). Although Si isotope fractionation factors between sil cate, and SiF_{4(g)} have not been determined experimentally, calculations based on infrared the site of isotope-substituted SiF_{4(g)} indicate large fractionation (at least 12.8‰), with ³⁰ si e, riched in the SiF_{4(g)} and depleted in the residual solid (Chemtob et al., 2015), i.e. fully con patible with our hypothesis.

In the Icelandic surface environment, the *P-III* ash deposited to the Jökulsá á Sólheimasandi river catchment likely experienced far-from-equilibrium conditions, with flow of fresh water through the porous ash deposit preventing oversaturation of solution with respect to secondary mineral phases. Under these conditions, and in the absence of significant concentrations of HCl, H₂SO₄ and/or HF in the water, the riverine δ^{30} Si was likely not influenced by Si-bearing

mineral precipitation or by Si-F complexation reactions (Ziegler et al., 2005; Chemtob et al., 2015). Additionally, in light of the near-zero fractionation factor of basalt dissolution in SiO₂undersaturated solutions (Chemtob et al., 2015), we contend that the best explanation for the low δ^{30} Si measured in the river on 8 May is surface-limited dissolution of a material already bearing a strongly ³⁰Si-depleted signature, as may be the case for the HF-affected *P-III* ash surfaces. The δ^{30} Si of the same river measured on 5 August, still low relative to typical values for Icelandic glacial rivers (Georg *et al.*, 2007), is consistent with the anomalous δ^{30} Si signal in the water decaying over time as dissolution advances into the ash bulk (which did not undergo Si volatilisation), and as some ash is removed from the river catchment.

We dismiss readily soluble silicon hexafluoride salts such as Na₂SiF₆, inferred to exist on *P*-*III* ash, as the driver of the anomalously low δ^{30} of value measured on 8 May in Jökulsá á Sólheimasandi river water. While the δ^{30} Si of such compounds is not known, SiF₆²⁻ formation originating with Si volatilisation (i.e. involving SiF_{4(g)}; reactions [6-9]) is accompanied by isotopic fractionation (Chemtob et *e*'., 2015), potentially leading to silicon hexafluoride salts with enriched δ^{30} Si values. However, upon deposition of *P*-*III* ash to the Jökulsá á Sólheimasandi river catchment these soluble compounds would have made a comparatively small contribution to the total riverine dissolved Si, so are unlikely to have affected the δ^{30} Si value recorded on 8 May. Moreover, they cannot explain the low δ^{30} Si value that persisted in this river on 5 August, almost three months after Eyjafjallajökull eruptive activity ended. Indeed, the absence of an elevated F² concentration in the Jökulsá á Sólheimasandi river on 5 August suggests that silicon hexafluoride salts from *P*-*III* ash were not contributing substantially to the chemistry of local surface waters at this time.

4.5 Animal health hazard

The formation of Na_2SiF_6 on ash bears implications for correctly assessing the health hazard, including fluorosis, posed to grazing livestock by F-rich magmatic eruptions. There is considerable evidence of toxic reactions in farm animals exposed to ashfall from earlier explosive unrest of Icelandic volcanoes, including Hekla, Askja and perhaps Krafla (Roholm, 1934; Roholm, 1937; Sigurdsson and Pálsson, 1957; Thorarinsson, 1967; Georgsson and Petursson, 1972). In an experimental study, Egyed and Shlosberg (1975) administered Na₂SiF₆ to one- to three-year-old sheep; the animals developed various symptoms of acute poisoning and died within six days of exposures $\geq 200 \text{ mg kg}^{-1}$ reported administered in the form of Na_2SiF_6 has a strong affinity for Ca^{2+} and Mg^{2-} and poisoning relates to the disruption of calcium metabolism. The corollary is that N_{a} , SiF₆ has the same acute toxicity as NaF in animals (Haneke and Carson, 2001) and is more toxic than Ca-containing fluoride salts such as CaF_2 and $CaSiF_6$ (Shupe and Alt're. 1/266). The lowest dose of F causing acute toxicity in sheep probably lies somew. are between 5 and 10 mg kg⁻¹ (Kristinsson et al., 1997). It can be easily shown that ingention of a few tens of grams of the P-II or P-III ash, quantities likely to be taken in during grazing (e.g., Field and Purves, 1964; Healy et al., 1966; Green et al., 1996), would have overexposed an adult sheep to F. We suggest that the presence of Na₂SiF₆ on ash hereases the health hazard posed to grazing livestock during and after an eruption.

5. Conclusions

The surface and leachate compositions of ash materials from the 2010 explosive activity of Eyjafjallajökull evidence that silicon hexafluoride salts, mostly Na_2SiF_6 , form on ash as a result of exposure to $HF_{(g)}$ in the eruption plume/cloud. As a large portion of the magmatic $HF_{(g)}$ emissions was scrubbed in the ice/meltwater-filled summit vent during the initial

phreatomagmatic eruptive phase, $HF_{(g/aq)}$ -ash reactions were only efficient during the subsequent purely magmatic activity of *P-II* and *P-III*. Consequently, the *P-II* and *P-III* ash represents a much stronger source of soluble F⁻ than the *P-I* ash. In addition, dissolution of the silicon hexafluoride salt(s) produces significant acidity in the leachates from these ash materials. More generally, we propose that such salts occur as the dominant F-bearing compounds on ash from purely magmatic eruptions and can explain the acidic pH values sometimes measured in the associated ash leachates.

The in-plume/cloud reactions involved in the deposition of filicen hexafluoride salts on ash leaves an altered surface enriched in ²⁸Si. The leaching and dissolution of ash deposits with such characteristics can temporarily modify the Si isotopic composition of runoff and surface water, as we observed for the Jökulsá á Sólheir and catchment directly affected by *P-III* ashfall. Thus, our study provides further ovidence that the presence of F during volcanic activity may influence silicate weathering processes and alter the direction and magnitude of any associated δ^{30} Si fractionation.

Being more toxic than CaF_2 , the termation of Na_2SiF_6 on ash has significance for assessing the hazard posed to grazing livestock during and after an eruption. We surmise that this compound played a major role in previous Icelandic cases of acute poisoning in sheep feeding in ash-impacted areas, and therefore advocate further monitoring and research of the biogeochemical effects of ash deposition in other volcanic regions where F-rich eruptions are known to occur.

Acknowledgements

This study was originally initiated through a NERC urgency grant (NE/1007636/1) when PD was affiliated with the University of York, UK. PD acknowledges the support of a FNRS MIS-Ulysse research grant (326.F.6001.11) for the subsequent research and analyses. PD is indebted to Peter Baxter for helping with ash and river sampling in May 2010, Claudine Givron and Anne Iserentant for technical assistance in the laboratory, and Paul Ayris for initiating the XPS measurements. Evgenia Ilyinskaya and Barbael Langmann donated additional ash samples. PD warmly thanks Niels Óskarssen for his helpful advice while conducting field work in April 2010. EM is supported by a Serrly Career Fellowship from the Leverhulme Trust and Isaac Newton Trust. FG and SQ are supported by FNRS mandate FC69480 and grant 26043653, respectively.

Author Contributions

All authors contributed. PD conceived the project. PD, JC and SJ collected the ash in Iceland. FG and SO carried out the silicon hotopic analyses. EM undertook the XPS measurements. PD and EM wrote the paper.

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TABLES AND FIGURES

	Eruption date	Sampling date	Location (UTM) Easting Northing	Distance from the volcano (km)
P-I				
EYJ-A19*	14-17/04/2010	23/04/2010	574929 7045094	12.7
EYJ-A40	17/04/2010	17/04/2010	559758 7046842	13.3
P-II				
EYJ-A8	23/04/2010	23/04/2010	543960 7057632	27.6
EYJ-A14	24/04/2010	24/04/2010	559698 705)128	11.3
P-III				
EYJ-A26	07/05/2010	07/05/2010	599256 7033811	37.7
EYJ-A30	06-07/05/2010	07/05/2010	583.)62 7041601	20.4
*composite sar	mple shielded from rai	n.		

Table 1. Details of the *P-I*, *P-II* and *P-III* ash samples.



Figure 1. Map showing field size locations for the ash (from *P-I* in pink, *P-II* in blue, *P-III* in green) and river water samples have map shows study area in Iceland.



Figure 2. Surface concentrations (in at.%) of F, Cl, Ca, Na and K in the *P-I*, *P-II* and *P-III* ash samples.



Figure 3. Concentrations of F⁻, Cl⁻, SO₄²⁻, Mg, Ca, Na and K in the *P-I*, *P-II* and *P-III* ash leachates. The dotted and plain bars indicate concentrations expressed in μ mol g⁻¹ and μ mol m⁻², respectively. 44



Figure 4. Isotopic composition (δ^{30} Si in ‰) of disso*trei*. Si and concentrations (in mmol l^{-1}) of dissolved F⁻ and Si in the Markarfljót (white svn.ools) and Jökulsá á Sólheimasandi (grey symbols) rivers sampled on 24 April, 8 May and 5 A 1gust 2010.

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Figure 5. Relative molar concentrations of SO_4^+ , Cl⁻ and F⁻ in the *P-I*, *P-II* and *P-III* ash leachates. The ternary diagram shows from the *P-II* and *P-III* ash materials are strongly enriched in F compared to the *P-I* ash, although they display roughly similar Cl:S ratios.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to infuence the work reported in this paper.