



## Controls on the surface chemical reactivity of volcanic ash investigated with probe gases



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### ABSTRACT

Increasing recognition that volcanic ash emissions can have significant impacts on the natural and human environment calls for a better understanding of ash chemical reactivity as mediated by its surface characteristics. However, previous studies of ash surface properties have relied on techniques that lack the sensitivity required to adequately investigate them. Here we characterise at the molecular monolayer scale the surfaces of ash erupted from Eyjafjallajökull, Tungurahua, Pinatubo and Chaitén volcanoes. Interrogation of the ash with four probe gases, trimethylamine (TMA;  $N(CH_3)_3$ ), trifluoroacetic acid (TFA;  $CF_3COOH$ ), hydroxylamine (HA;  $NH_2OH$ ) and ozone ( $O_3$ ), reveals the abundances of acid–base and redox sites on ash surfaces. Measurements on aluminosilicate glass powders, as compositional proxies for the primary constituent of volcanic ash, are also conducted. We attribute the greater proportion of acidic and oxidised sites on ash relative to glass surfaces, evidenced by comparison of TMA/TFA and HA/ $O_3$  uptake ratios, in part to ash interaction with volcanic gases and condensates (e.g.,  $H_2O$ ,  $SO_2$ ,  $H_2SO_4$ , HCl, HF) during the eruption. The strong influence of ash surface processing in the eruption plume and/or cloud is further supported by particular abundances of oxidised and reduced sites on the ash samples resulting from specific characteristics of their eruptions of origin. Intense interaction with water vapour may result in a higher fraction of oxidised sites on ash produced by phreatomagmatic than by magmatic activity. This study constitutes the first quantification of ash chemical properties at the molecular monolayer scale, and is an important step towards better understanding the factors that govern the role of ash as a chemical agent within atmospheric, terrestrial, aquatic or biotic systems.

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### 1. Introduction

A broad scientific community is interested in better understanding the role of past and present volcanic activity in eliciting environmental changes. Notably, there is growing evidence that emissions of ash, generated by explosive eruptions and consisting of particles <2 mm in diameter comprised of aluminosilicate glass and crystalline minerals, can considerably influence biogeochemical processes involving key elements such as C, Fe and S from local to perhaps global scales (Ayris and Delmelle, 2012 and references therein; Cather et al., 2009; Olgun et al., 2011). Similar to airborne mineral dust particles (Usher et al., 2003), ash emissions may also temporarily affect the chemical composition of the atmosphere by interacting with significant trace gases including  $SO_2$ ,

$O_3$ ,  $NO_x$  and organic compounds (Maters, 2016). In addition, exposure to ash has long been alleged to pose a hazard to human respiratory health (Horwell and Baxter, 2006).

Arguably, the surface chemical and physical properties of ash play a fundamental role in dictating its environmental and health impacts since these are mediated by interfacial solid–liquid or solid–gas reactions. In general, the surfaces of crystalline and amorphous solids are imperfect as they feature various defects (e.g., lattice defects, non-stoichiometry, impurity ions, dislocations). These defects confer to the solid surface a chemical reactivity. By the same token, ash, being composed of crystals and glass, displays a heterogeneous distribution of surface sites potentially active in various interfacial reactions. For over forty years, studies of ash surface chemistry have been typified by the investigation of sulphate and halide salt deposits on ash. Although ash leachate analysis remains a primary characterisation tool, recent studies have deployed increasingly surface-sensitive analytical techniques including X-ray photoelectron spectroscopy (XPS) and atomic force

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**Table 1**  
Details of the samples used in this study.

| Material | Source volcano   | Sample code | Eruption date <sup>a</sup> | Eruption type <sup>a</sup> | Classification <sup>b</sup> | SSA <sub>BET</sub> <sup>c</sup><br>(m <sup>2</sup> g <sup>-1</sup> ) | Bulk glass content <sup>d</sup><br>(wt.%) |
|----------|------------------|-------------|----------------------------|----------------------------|-----------------------------|--|---|
| Glass    | Etna             | TRB         | –                          | –                          | Trachybasalt                | 0.3  | 100                                       |
|          | Tungurahua       | AND         | –                          | –                          | Andesite                    | 0.2  | 100                                       |
|          | Unzen            | DCT         | –                          | –                          | Dacite                      | 0.3  | 100                                       |
|          | Lipari           | RHY         | –                          | –                          | Rhyolite                    | 0.5  | 100                                       |
| Ash      | Eyjafjallajökull | EYJA        | 17 April 2010              | Phreatomagmatic            | Trachyandesite              | 7.5  | 56  |
|          | Tungurahua       | TUNG        | 23 Aug. 2012               | Magmatic                   | Andesite                    | 1.8  | 45  |
|          | Pinatubo         | PIN         | 15 June 1991               | Magmatic                   | Andesite                    | 1.5  | 60  |
|          | Chaitén          | CHAI        | 2 May 2008                 | Magmatic                   | Rhyolite                    | 0.5  | 76  |

<sup>a</sup> The glass samples were synthesised in the laboratory from volcanic rock – melted, homogenised, quenched and crushed – and as such can no longer be associated with an individual eruption. The ash eruption types come from Gudmundsson et al. (2012), A. Guevara, pers. comm. (April 2013), Koyaguchi (1996), and Castro and Dingwell (2009), respectively.

<sup>b</sup> According to the Total Alkali Silica diagram (Le Maitre et al., 2002) based on bulk composition (Table S1 in the Supporting Information, SI).

<sup>c</sup> Uncertainty in duplicate measurements is  $\pm 5\%$ .

<sup>d</sup> Accuracy is estimated to be in the range of 5–10% based on analysis of synthetic mixtures comprised of two crystalline phases and volcanic glass.

**Table 2**  
Surface compositions of the samples used in this study, expressed as at.%.  
n.d.: not detected.

| Material | Sample <sup>a</sup> | O    | Si   | Al   | Fe  | Mg   | Ca  | Na  | K   | Ti   | Cl   | F    | S    |
|----------|---------------------|------|------|------|-----|------|-----|-----|-----|------|------|------|------|
| Glass    | TRB                 | 55.9 | 21.9 | 10.1 | 1.9 | 3.0  | 3.1 | 2.5 | 0.9 | 0.4  | 0.1  | 0.2  | n.d. |
|          | AND                 | 55.3 | 26.3 | 9.8  | 1.3 | 2.4  | 2.1 | 2.0 | 0.7 | 0.2  | n.d. | n.d. | n.d. |
|          | DCT                 | 55.3 | 28.7 | 9.2  | 0.8 | 1.5  | 1.6 | 1.7 | 1.0 | 0.2  | n.d. | n.d. | n.d. |
|          | RHY                 | 56.9 | 31.4 | 7.0  | 0.3 | n.d. | 0.3 | 2.2 | 1.8 | n.d. | n.d. | n.d. | n.d. |
| Ash      | EYJA                | 56.4 | 25.5 | 7.2  | 3.0 | 3.4  | 1.5 | 1.4 | 0.5 | 0.5  | 0.3  | 0.3  | n.d. |
|          | TUNG                | 56.7 | 30.7 | 7.2  | 0.8 | 0.8  | 1.3 | 1.3 | 0.5 | 0.2  | 0.2  | 0.3  | n.d. |
|          | PIN                 | 54.8 | 31.2 | 8.4  | 0.7 | 2.0  | 0.8 | 1.0 | 0.9 | n.d. | 0.1  | 0.2  | n.d. |
|          | CHAI                | 60.2 | 29.8 | 7.0  | 0.3 | 0.4  | 0.8 | 1.2 | 0.2 | n.d. | 0.1  | n.d. | n.d. |

<sup>a</sup> TRB: trachybasalt, AND: andesite, DCT: dacite, RHY: rhyolite, EYJA: Eyjafjallajökull, TUNG: Tungurahua, PIN: Pinatubo, CHAI: Chaitén. Concentrations normalised to 100%. n.d.: not detected.

microscopy (Delmelle et al., 2007; Gislason et al., 2011). However, these approaches are hampered by a limited sensitivity for surface species and cannot provide qualitative and quantitative information on the interfacial composition.

Here we use for the first time a non-invasive analytical technique to provide direct insight at the molecular monolayer scale into the chemical functional groups, comprised of acidic, basic, reduced and oxidised sites, that occur on volcanic ash surfaces. This highly surface-sensitive technique involves interrogation of a solid substrate by means of heterogeneous titration with a selected suite of probe gases using a Knudsen flow reactor (Caloz et al., 1997). Samples of ash from different explosive eruptions are investigated. To enhance understanding of the factors that control the nature and abundance of chemical functional groups on ash surfaces, we also use powdered aluminosilicate glasses as compositional proxies for the primary constituent of ash (Heiken and Wohletz, 1992). We demonstrate that our new experimental approach delivers unprecedented qualitative and quantitative insights into chemical functional groups on ash which, in turn, furthers knowledge of the factors that modulate ash surface reactivity.

## 2. Materials and methods

### 2.1. Glass and ash samples

Eight powdered glass and ash samples from rhyolitic to trachybasaltic in composition, chosen to broadly span a range of ash compositions produced during volcanic activity, were used in this study (Table 1). The glass samples were synthesised by melting volcanic rocks at 1300 to 1600 °C, homogenising and then quenching the melts, and crushing the solid glasses to powder. The ash samples derive from different volcanic eruptions and, with the exception of Pinatubo ash (PIN), have not been exposed to rain or snow prior to collection. The specific surface area (SSA<sub>BET</sub> in

m<sup>2</sup>g<sup>-1</sup>) of the samples, after overnight degassing at 150 °C to remove surface adsorbed water, was obtained from a five-point Kr adsorption isotherm at –196 °C based on the Brunauer, Emmet and Teller (BET) model (Brunauer et al., 1938) using a Micromeritics ASAP 2000 surface area analyser. The proportion of glassy (amorphous) material in the volcanic ash was determined by X-ray powder diffraction (XRD) with a Cu<sub>K $\alpha$</sub>  X-ray beam using a Bruker D8 Advance instrument and the SIROQUANT 4.0 software program. Briefly, this involved grinding the ash and spiking it with a known mass (10 wt.%) of crystalline internal standard, corresponding here to Si powder, to quantify amorphous content in the samples as per Ward and French (2006).

The composition of the samples in the topmost two to ten nanometers of the surface (Table 2), in terms of relative concentrations (in at.%) of O, Si, Al, Fe, Mg, Ca, Na, K, Ti, Cl, F and S, was analysed by XPS using a Kratos Axis Ultra instrument with a monochromatic Al<sub>K $\alpha$</sub>  X-ray beam centered at 1486.6 eV. The binding energy scale was calibrated by assigning a value of 284.8 eV to the C 1s peak for adventitious carbon (Genet et al., 2008).

### 2.2. Knudsen flow reactor experiments

A Knudsen flow reactor operating under high vacuum (<0.1 Pa) was used to measure the reactive uptake of various probe gases (see section 2.3) on volcanic glass and ash. The pioneering use of a Knudsen apparatus for the study of chemical reactions is discussed by Golden et al. (1973) and its adaptation to the study of heterogeneous chemistry is detailed by Fenter et al. (1994) and Caloz et al. (1997). Briefly, a Knudsen flow reactor operates at very low pressures and in the molecular flow regime, i.e., the mean free path of the gas is typically three to ten times the diameter of the escape aperture. The method relies on measuring the rate of disappearance of a gas when exposed to a substrate (i.e., here a powdered

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