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Key Points:

- Sulfur dioxide and ozone are taken up on volcanic glass/ash at ambient temperature likely at basic and reducing surface sites, respectively
- A typically lower ash reactivity toward these gases may reflect exposure to acidic and oxidizing conditions in the volcanic plume/cloud
- Measured uptake capacity and coefficient values suggest that ash emissions may represent a sink for atmospheric sulfur dioxide and ozone

Supporting Information:

- Supporting Information S1

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Reactive Uptake of Sulfur Dioxide and Ozone on Volcanic Glass and Ash at Ambient Temperature

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Abstract The atmospheric impacts of volcanic ash from explosive eruptions are rarely considered alongside those of volcanogenic gases/aerosols. While airborne particles provide solid surfaces for chemical reactions with trace gases in the atmosphere, the reactivity of airborne ash has seldom been investigated. Here we determine the total uptake capacity (N_i^M) and initial uptake coefficient (γ_M) for sulfur dioxide (SO_2) and ozone (O_3) on a compositional array of volcanic ash and glass powders at ~25°C in a Knudsen flow reactor. The measured ranges of N_i^{SO2} and γ_{SO2} (10^{11}–10^{13} molecules cm^{-2} and 10^{-3}–10^{-2}) and N_i^{O3} and γ_{O3} (10^{12}–10^{13} molecules cm^{-2} and 10^{-3}–10^{-2}) are comparable to values reported for mineral dust. Differences in ash and glass reactivity toward SO_2 and O_3 may relate to varying abundances of, respectively, basic and reducing sites on these materials. The typically lower SO_2 and O_3 uptake on ash compared to glass likely results from prior exposure of ash surfaces to acidic and oxidizing conditions within the volcanic eruption plume/cloud. While sequential uptake experiments overall suggest that these gases do not compete for reactive surface sites, SO_2 uptake forming adsorbed S(IV) species may enhance the capacity for subsequent O_3 uptake via redox reaction forming adsorbed S(VI) species. Our findings imply that ash emissions may represent a hitherto neglected sink for atmospheric SO_2 and O_3.

1. Introduction

The average annual load of volcanic ash to the atmosphere (176–256 Tg a^{-1}) (Durant et al., 2010) provides a total solid surface area on the order of 1.8 to 2.6 × 10^8 km^2 (assuming an ash specific surface area of 1 m^2 g^{-1}) (Delmelle et al., 2005), equivalent to one third to one half of the Earth's geometric surface area. A single Plinian eruption such as the 1991 Pinatubo eruption generates an ash mass (e.g., ~3000 Tg) (Koyaguchi, 1996) with a solid surface area reaching over ten times this amount. Maters et al. (2016) have recently confirmed the presence of reactive surface sites on volcanic ash and glass, and similar to wind blown mineral dust from arid and semiarid regions (1000–3000 Tg a^{-1} emitted) (Matsuki et al., 2005; Penner et al., 2001; Usher et al., 2003), airborne ash surfaces may take part in heterogeneous reactions with trace atmospheric gases such as SO_2, O_3, NO_x, and organic compounds.

While the impact of volcanic activity on atmospheric chemistry is traditionally studied in relation to sulfur and halogen emissions (e.g., Brasseur et al., 1990; Robock, 2000; von Glasow et al., 2009), the potential of aluminosilicate ash from explosive eruptions to influence atmospheric chemistry remains unknown. Amid growing recognition of O_3 depletion in the vertical volcanic plume and/or the laterally dispersed volcanic cloud (e.g., Roberts et al., 2009; Surl et al., 2015; von Glasow, 2010), the role of ash particles has been dismissed (Vance et al., 2010). However, this conclusion was based on an assumed low reactivity of ash toward O_3 and prompts reconsideration as ash-O_3 interaction has not been investigated before now. Moreover, although it has been suggested that a short residence time of airborne ash limits its atmospheric/climatic impact relative to volcanic gases and aerosols (e.g., Niemeier et al., 2009; Robock, 2000), recent evidence of ash suspended aloft for several months (Vernier et al., 2016) calls for a more careful assessment of its potential effects.

Therefore, in light of the intermittent yet non-negligible presence of ash surfaces in the atmosphere, quantitative constraints on ash-gas reactivity are essential to improve understanding of the capacity of ash to act as a source of/sink for trace atmospheric species. In addition to affecting atmospheric chemistry, heterogeneous reactions can modify the physicochemical characteristics (e.g., hygroscopicity) of particle

Table 1
Details of the Volcanic Glass and Ash Samples Used in This Study

	Material							
	Glass				Ash			
Sample code	TRB	AND	DCT	RHY	EYJA	TUNG	PIN	CHAI
Source volcano	Etna	Tungurahua	Unzen	Lipari	Eyjafjallajökull	Tungurahua	Pinatubo	Chaitén
Eruption date[a]	-	-	-	-	17 April 2010	23 August 2012	15 June 1991	2 May 2008
Classification[b]	Trachybasalt	Andesite	Dacite	Rhyolite	Trachyandesite	Andesite	Andesite	Rhyolite
SSA_{BET} ($m^2\ g^{-1}$)[c]	0.3	0.2	0.3	0.5	7.5	1.8	1.5	0.5
Bulk glass content (wt %)[d]	100	100	100	100	56	45	60	76

[a] The glass samples were generated in the laboratory from volcanic rock (melted, homogenized, quenched, and crushed) and therefore are no longer associated with an individual eruption. [b] According to the Total Alkali Silica diagram (Le Maitre et al., 2002) based on bulk composition (Table S1). [c] Uncertainty in duplicate measurements is ±5%. [d] Accuracy is estimated to be in the range of 5–10% based on analysis of artificial mixtures comprised of volcanic glass and two crystalline phases.

surfaces, in turn, influencing their impact on radiation, cloud properties, and thereby ultimately climate (e.g., Wurzler et al., 2000). The present study quantifies for the first time the reactivity of volcanic ash toward gaseous SO_2 and O_3 at ambient temperature. Using a low-pressure flow reactor, we determine the total uptake capacity and initial uptake coefficient of SO_2 and O_3 on a compositional array of natural ash and synthetic aluminosilicate glass powders, the glass serving as a proxy for the dominant constituent of ash.

2. Materials and Methods

2.1. Volcanic Glass and Ash Samples

Eight powdered glass and ash samples from trachybasaltic to rhyolitic in composition, broadly spanning a range of compositions produced during volcanic activity, were used in this study (Table 1). Details on the origin of these materials and on their physicochemical characterization are given in Maters et al. (2016). The surface elemental composition of the samples is provided in the supporting information (SI; Table S1).

2.2. Knudsen Flow Reactor Experiments

Ash is exposed to magmatic SO_2 within the volcanic eruption plume/cloud as well as atmospheric SO_2 upon mixing with ambient air. The latter process also brings ash into contact with atmospheric oxidizing agents such as $O_{3.}$ Thus, measurements of SO_2 and O_3 uptake in isolation and in sequence (SO_2 followed by O_3) on the glass and ash material were carried out.

All experiments were conducted at ambient temperature (~25°C) in a Knudsen flow reactor operating under high vacuum (<0.1 Pa) in the molecular flow regime (Caloz et al., 1997; Golden et al., 1973). The key principles of the Knudsen apparatus as applied to study heterogeneous reactions on volcanic glass and ash are described in Maters et al. (2016). Details on the reactor parameters and the experimental protocol used for uptake measurements appear in the SI (Table S2 and Text S2). Briefly, the technique relies on measuring the rate of gas disappearance when exposed to a substrate (here a powdered solid) within the reactor relative to the rate of gas effusion from the reactor through an escape aperture. An experiment involves recording the mass spectrometer signal intensity of a parent or fragment ion before, during, and after gas exposure to the substrate.

The total number of gas molecules M taken up on the sample N_i^M is calculated according to

$$N_i^M = \int \left(F_i^M - F^M(t)\right)dt \qquad \text{(integration limits between } t_0 \text{ and } t_s\text{)} \tag{1}$$

where F_i^M and $F^M(t)$ correspond to the measured molecular flow rates of the gas entering and exiting the reactor, respectively, and the integration period from t_0 to t_s represents the time interval taken for the gas to saturate the sample surface, i.e., when the experimentally measured uptake becomes negligible and $F^i_M = F_M(t)$. The calculated N_i^M value is normalized by the Brunauer-Emmett-Teller (BET) surface area (calculated from the BET specific surface area; Table 1) of the sample in order to give number of gas molecules taken up per square centimeter of its surface (i.e., to account for differences in the total available area presented by the sample surfaces).

The reaction kinetics can be represented in two ways assuming a first-order rate law for adsorption. The first is a heterogeneous rate constant k_{het}, which depends on the effusion rate constant k_{esc} and is unique to the specific measurement system, whereas the second is a dimensionless uptake probability or coefficient γ_M, which has been normalized by the surface-to-volume ratio A_s/V of the system and is therefore a transferable parameter. The uptake coefficient is defined as the fractional collision probability of gas molecule M loss to the sample surface per unit time. These kinetic parameters are calculated as follows:

$$k_{het} = (I_o/I\text{-}1)/k_{esc} \tag{2}$$

$$\gamma_M = k_{het}/\omega = (I_o/I\text{-}1)(A_h/A_s) = k_{het}4V/(cA_s) \tag{3}$$

where I_o and I are the measured amplitudes of the mass spectrometer signal when the sample is isolated and exposed, respectively, A_h is the surface area of the escape aperture, A_s is the geometric surface area of the sample plate, V is the volume of the flow reactor, and ω is the collision frequency of the average gas molecule moving at a mean molecular speed c with the sample surface.

3. Results

The mass spectrometer signal intensity for SO_2 or O_3 immediately decreased upon gas exposure to the glass or ash material and then recovered over tens of seconds to several minutes toward a steady state level equivalent to the initial signal intensity (e.g., Figures 1a and 1b).

3.1. Sulfur Dioxide Uptake

The total number of SO_2 molecules taken up per unit surface area (N_i^{SO2}) and the initial SO_2 uptake coefficient (γ_{SO2}) of the glass and ash samples in each experiment are listed in Table S3.

3.1.1. Total SO_2 Uptake Capacity

Values of N_i^{SO2} for each sample are displayed as a function of surface Si content in Figure 2a. The glass samples exhibited N_i^{SO2} values on the order of 10^{13} molecules cm^{-2}, with the lowest and highest corresponding to the compositional end-members rhyolite and trachybasalt glass (0.8–1.6 and 5.7–6.3 × 10^{13} molecules cm^{-2}, respectively). The ash samples exhibited N_i^{SO2} values ranging from middle 10^{11} to low 10^{13} molecules cm^{-2}, with the lowest corresponding to Chaitén and Tungurahua ash (5.8–6.2 and 5.9–12 × 10^{11} molecules cm^{-2}, respectively) and highest corresponding to Pinatubo and Eyjafjallajökull ash (3.9–6.7 × 10^{12} and 1.2–1.8 × 10^{13} molecules cm^{-2}, respectively).

3.1.2. Initial SO_2 Uptake Coefficient

Values of γ_{SO2} for each sample are shown as a function of surface Si content in Figure 2b. Within the glass data set, the rhyolite and trachybasalt glass compositional end-members displayed the lowest and highest γ_{SO2} values (1.0–1.7 and 3.6–4.5 × 10^{-2}, respectively), although the former range is nearly indistinguishable from

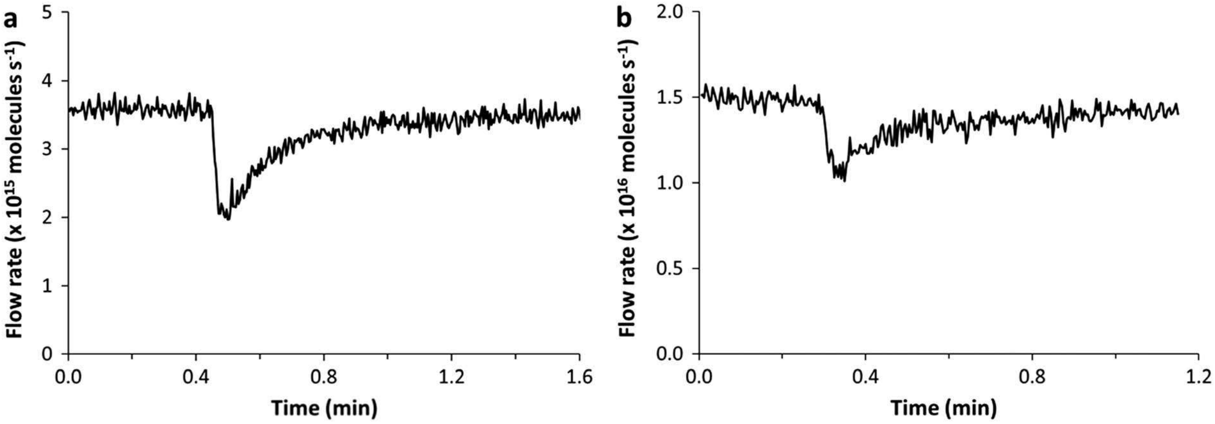

Figure 1. Mass spectrometer signal intensity (a) at m/e 64 as a function of time during exposure of 248 mg of andesite glass to SO_2 gas at a concentration of 1.6 × 10^{12} molecules cm^{-3} and (b) at m/e 48 as a function of time during exposure of 130 mg of Eyjafjallajökull ash to O_3 gas at a concentration of 6.0 × 10^{12} molecules cm^{-3}.

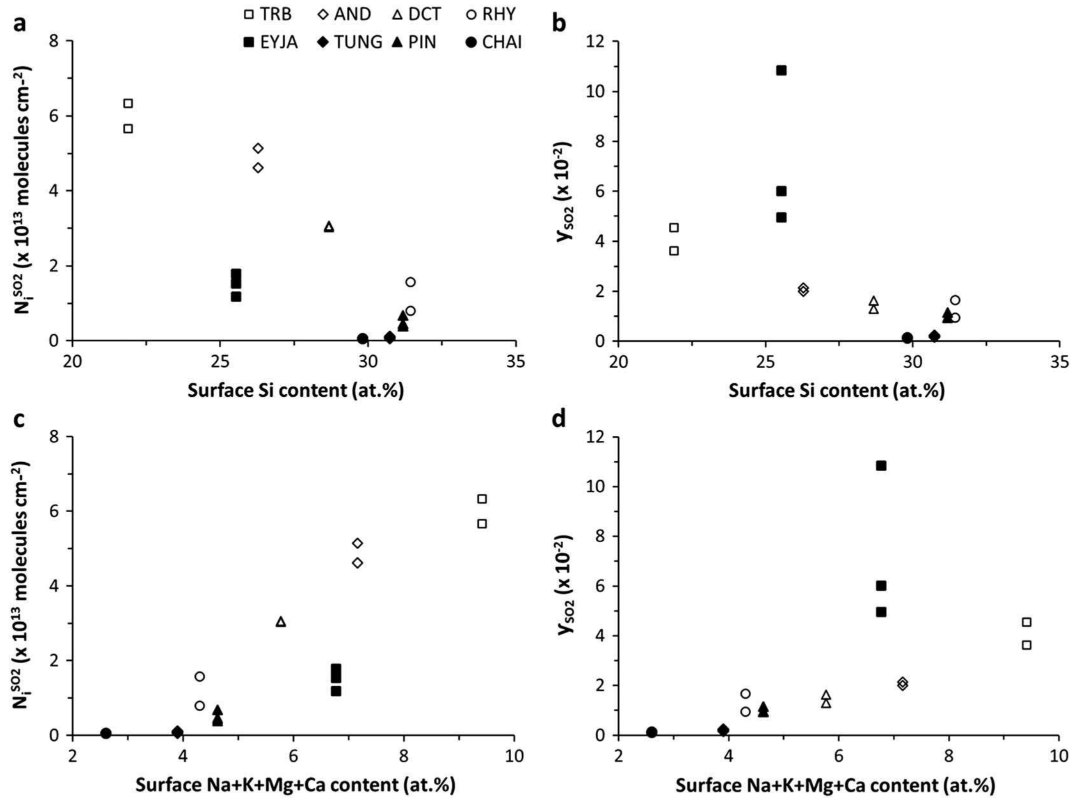

Figure 2. (a) Total SO_2 uptake capacity (N_i^{SO2}) and (b) initial SO_2 uptake coefficient (γ_{SO2}) versus surface Si content of the glass and ash samples. (c) Total SO_2 uptake capacity (N_i^{SO2}) and (d) initial SO_2 uptake coefficient (γ_{SO2}) versus surface Na + K + Mg + Ca content of the glass and ash samples. TRB: trachybasalt glass, AND: andesite glass, DCT: dacite glass, RHY: rhyolite glass. EYJA: Eyjafjallajökull ash, TUNG: Tungurahua ash, PIN: Pinatubo ash, CHAI: Chaitén ash.

that of the dacite glass. Within the ash data set, the Pinatubo and Eyjafjallajökull ash displayed the highest γ_{SO2} values (0.9–1.1 and 5.0–10.8 × 10^{-2}, respectively); comparable to the range exhibited by the glass material. In contrast, the Chaitén and Tungurahua ash γ_{SO2} values (1.3–1.5 and 1.6–2.4 × 10^{-3}, respectively) were up to an order of magnitude lower.

3.2. Ozone Uptake

The total number of O_3 molecules taken up per unit surface area (N_i^{O3}) and the initial O_3 uptake coefficient (γ_{O3}) of the glass and ash material in each experiment are given in Table S4.

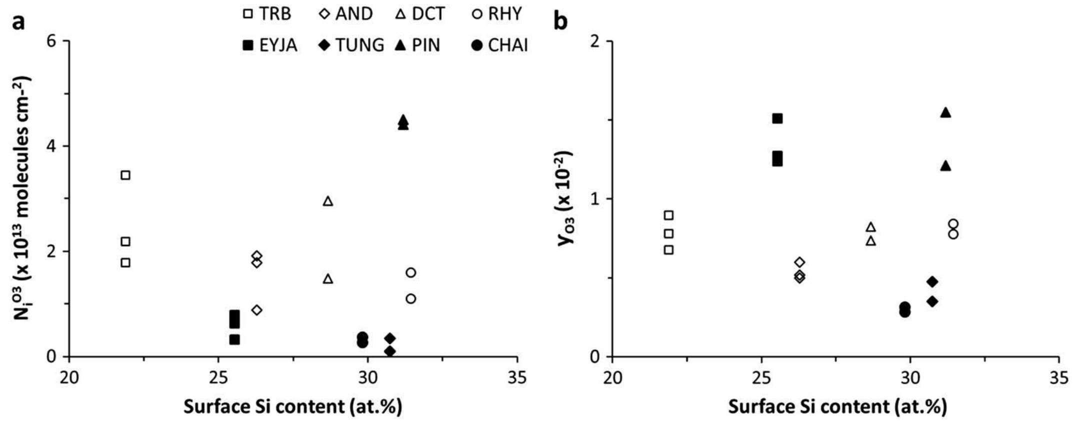

Figure 3. (a) Total O_3 uptake capacity (N_i^{O3}) and (b) initial O_3 uptake coefficient (γ_{O3}) versus surface Si content of the glass and ash samples. Sample codes as in Figure 2.

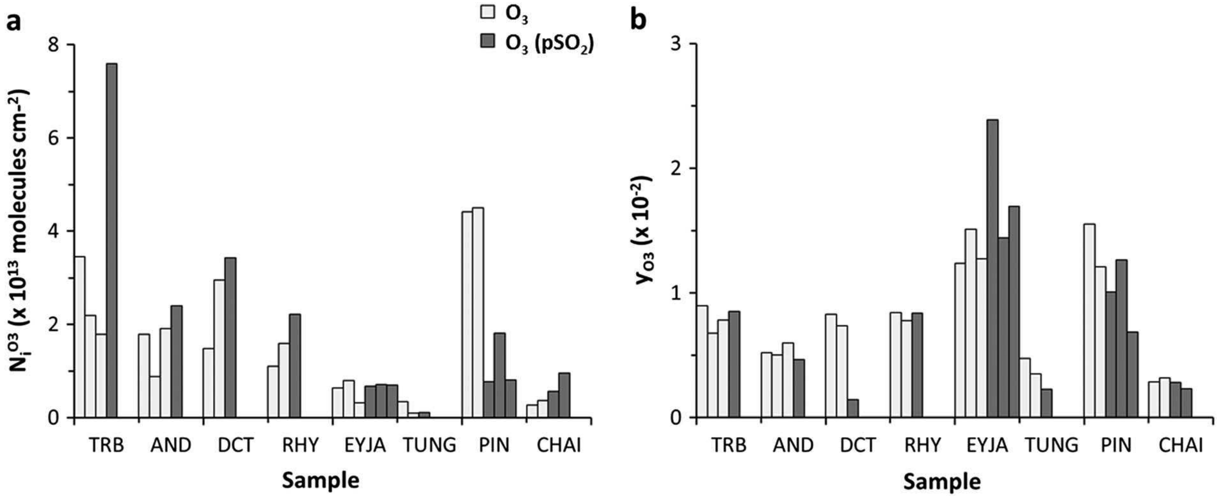

Figure 4. (a) Total O_3 uptake capacity (N_i^{O3}) and (b) initial O_3 uptake coefficient (γ_{O3}) for the original and SO_2 pre-exposed (pSO_2) glass and ash samples. Sample codes as in Figure 2.

3.2.1. Total O_3 Uptake Capacity

Values of N_i^{O3} for each sample are presented as a function of surface Si content in Figure 3a. The N_i^{O3} values range from 0.9 to 3.4 × 10^{13} molecules cm^{-2} for the glass and 0.9 to 7.9 × 10^{12} molecules cm^{-2} for the ash, except Pinatubo ash which displayed the highest N_i^{O3} values of 4.4 to 4.5 × 10^{13} molecules cm^{-2} across all samples.

3.2.2. Initial O_3 Uptake Coefficient

Values of γ_{O3} for each sample are plotted as a function of surface Si content in Figure 3b. All samples exhibited γ_{O3} values in the range of low 10^{-3} to low 10^{-2}, with the glass and ash broadly comparable, although Pinatubo and Eyjafjallajökull ash showed notable γ_{O3} values up to 6 times greater than those of the other samples.

3.3. Ozone Uptake on Sulfur Dioxide-Exposed Samples

The N_i^{O3} and γ_{O3} values of the SO_2-exposed glass and ash in each experiment are provided in Table S5.

Figure 4a shows the N_i^{O3} values for samples exposed only to O_3 and those exposed to SO_2 and subsequently to O_3. For the glass samples, previous SO_2 exposure slightly increased N_i^{O3}; by a factor of 1.5 to 3 on average, but a robust statistical analysis is not possible due to the small sample size. In contrast, previous exposure of the ash samples to SO_2 did not exert a consistent influence on N_i^{O3}, although Pinatubo ash exhibited a notable decrease by a factor of 4 on average in N_i^{O3} after SO_2 exposure.

Figure 4b shows the γ_{O3} values for samples exposed only to O_3 and those exposed to SO_2 and then to O_3. Overall, no significant effect of prior SO_2 exposure on γ_{O3} for the glass or ash samples is apparent. However, the dacite glass displayed a decrease by a factor of almost 6 in γ_{O3} when previously exposed to SO_2.

4. Discussion

4.1. Sulfur Dioxide Uptake

All volcanic glass and ash samples were reactive toward SO_2 gas (Table S3).

The N_i^{SO2} of the glass samples decreases with their surface Si content (Figure 2a). The γ_{SO2} roughly follows the same tendency (Figure 2b). This conforms with previous findings that gaseous SO_2 is relatively unreactive toward silica (SiO_2). For example, Usher et al. (2002) measured a lower SO_2 uptake on SiO_2 than on MgO, Al_2O_3, Fe_2O_3, and TiO_2 mineral powders, whereas Farges et al. (2009) observed no to little SO_2 adsorption on quartz and pure SiO_2 glass, in contrast to multicomponent glasses. On the other hand, the N_i^{SO2} of the glasses studied here increases with their total surface Na, K, Mg, and Ca content (Figure 2c). The γ_{SO2} broadly exhibits a similar tendency (Figure 2d). This likely reflects a role of basic surface sites associated with these elements in SO_2 adsorption (e.g., $SO_{2(g)} + -Mg\text{-}OH_{(s)} \rightarrow -Mg\text{-}OS\text{-}O_2\text{-}H_{(s)}$) (Zhang et al., 2006). Accordingly, N_i^{SO2} increases with the total basic site abundance on the glass samples as independently revealed by the strongly acidic probe gas trifluoroacetic acid (i.e., N_i^{TFA}) (Maters et al., 2016) (Figure S1). Since SO_2 is a weakly acidic gas, its uptake is thought to occur on strongly basic sites representing a subset of all basic sites interacting with TFA and affiliated with alkali and alkaline earth metals at the surface. Semiquantitative comparison of these data suggests that strongly basic sites (N_i^{SO2}) make up ~20% of total basic sites (N_i^{TFA}) on the glass samples (Figure S1).

Sulfur dioxide chemisorption at basic sites may involve reaction with oxide anions (O^{2-}) or hydroxyl groups (OH^-), leading to formation of surface S(IV) species (Goodman et al., 2001; Karge & Dalla Lana, 1984; Pacchioni et al., 1994; Waqif et al., 1992). Sulfite (SO_3^{2-}) and bisulfite (HSO_3^-) have been detected by various spectroscopic techniques on natural dust, mineral oxide, and aluminosilicate glass powders exposed to SO_2 gas (e.g., Farges et al., 2009; Goodman et al., 2001; Ullerstam et al., 2002; Usher et al., 2002; Zhang et al., 2006). As volcanic glass and ash have been shown to contain basic surface sites (Maters et al., 2016), SO_2 chemisorption forming SO_3^{2-}/HSO_3^- likely occurred on these materials in the Knudsen flow reactor. Importantly, no SO_2 desorption was measured after stopping the gas flow and no secondary SO_2 uptake was observed upon sample reexposure to the gas flow, indicating that SO_2 uptake was irreversible on the glass and ash on the timescale of our measurements. Aqueous leachates of the original glass samples and a subset of those exposed to SO_2 support the formation of SO_3^{2-} on the latter, as dissolved SO_3^{2-} was not detected in leachates of the original glasses but was present in those of the exposed glasses (Text S3 and Table S6). Additionally, the rank of SO_3^{2-} concentrations measured in the exposed glass leachates follows the rank of N_i^{SO2} values determined for the glass samples in the Knudsen flow reactor, i.e., trachybasalt > andesite > dacite > rhyolite (Figure 2a and Table S3).

Similar to the glass materials, the N_i^{SO2} and γ_{SO2} of the ash samples may show a dependence on total surface Na, K, Mg, and Ca content, although the relationship appears to be less clear (Figures 2c and 2d). A *t* test performed on the glass and ash N_i^{SO2} data sets also confirms that the mean normalized SO_2 uptake (i.e., N_i^{SO2}/Na + K + Mg + Ca content) for the glass samples exceeds that for the ash samples ($P < 0.001$). Moreover, on the ash materials N_i^{SO2} does not increase with the total basic site abundance as revealed by uptake of the probe gas TFA (i.e., N_i^{TFA}) (Maters et al., 2016) (Figure S1). Since SO_2 and TFA react with basic sites of different strengths, this suggests that in contrast to the glasses, the relative abundance of strongly versus weakly basic sites varies widely for the ash specimens. This is exemplified by the dominance of weakly basic sites on Chaitén ash and strongly basic sites on Eyjafjallajökull ash (Figure S1). Altogether, these disparate trends in SO_2 uptake by the glass and ash samples, including the overall lower N_i^{SO2} of the latter (Table S3), may relate to the presence of crystalline mineral phases in ash and/or to the distinct surface generation and alteration histories of the glass and ash materials (Maters et al., 2016).

Farges et al. (2009) argue that SO_2 adsorption on volcanic ash is most likely to occur on glassy regions of its surface, based on observations of higher SO_2 uptake on SiO_2 glass than on quartz. However, this conclusion neglects the importance of alkali and alkaline earth atoms in generating basic surface sites, and presently, we have no basis to infer that the abundances of strongly basic sites for SO_2 uptake differ on amorphous versus crystalline aluminosilicates. While the SO_2 uptake on the four ash samples studied here shows no trend according to bulk glass content (Figure S2), without knowledge of how amorphous and crystalline phases within ash are actually distributed at the solid surface, we can neither confirm nor refute an influence of crystallinity on SO_2 uptake by ash.

The glass and ash also differ fundamentally in terms of prior ash interaction with acidic gases and condensate during transit through the volcanic plume/cloud. Partial removal/neutralization of basic surface sites (e.g., Digne et al., 2008; Zhang et al., 2002) and, relatedly, exposure to gaseous SO_2 during the eruption probably explain the lower and more variable SO_2 uptake on the natural ash compared to the synthetic glass in this study. Reaction with SO_2 at high temperature in the plume produces ash surfaces bearing SO_4^{2-} salts (e.g., $CaSO_4$, Na_2SO_4) (Ayris et al., 2013) and therefore likely containing fewer sites for additional SO_2 uptake in the Knudsen flow reactor. Convincingly, aqueous leachates of the original ash samples indicate the presence of S species (e.g., SO_4^{2-}) already on the erupted material (Text S4 and Table S7). The remarkably high dissolved SO_4^{2-} content of the Chaitén ash leachate may point to extensive prior ash-SO_2 interaction in the Chaitén plume. This could partly explain the particularly low relative abundance of strongly basic sites on Chaitén ash (Figure S1) and conforms with its low SO_2 uptake measured here (Table S3). Judeikis et al. (1978) similarly hypothesized that reaction of fly ash with SO_2 at high temperature within the coal-fired emission source lowers its capacity for subsequent experimental SO_2 uptake, i.e., compared to the same ash pre-rinsed to remove soluble S species. Thus, partial consumption of reactive sites on ash surfaces already near the point of emission may diminish heterogeneous SO_2 removal in the atmosphere.

4.2. Ozone Uptake

As for SO_2 gas, all volcanic glass and ash samples were reactive toward O_3 gas (Table S4).

Neither the glass nor the ash show a relationship between N_i^{O3} or γ_{O3} and surface chemical composition (e.g., Figures 3a and 3b). Others have suggested a compositional influence on O_3 uptake by mineral oxides and natural dust, decreasing in the order $Fe_2O_3 > Al_2O_3 > SiO_2 >$ kaolinite, with Saharan sand and Chinese loess near the lower end of this rank, although this trend is not well understood (Hanisch & Crowley, 2003; Michel et al., 2003; Suzuki et al., 1979). Reactive O_3 uptake on such substrates may consist of dissociative adsorption, possibly involving Lewis acid sites, resulting overall in catalytic O_3 decomposition and O_2 production (Bulanin et al., 1995; Golodets, 1983; Thomas et al., 1997). This reportedly proceeds by (i) relatively fast O_3 adsorption leading to surface bound O and gaseous O_2, (ii) secondary O_3 adsorption forming surface bound peroxide (O_2^{2-}) and gaseous O_2, and finally, (iii) slow decomposition of surface bound O_2^{2-} and/or recombination of two surface bound Os, resulting in O_2 desorption and hence, regeneration of reactive surface sites (Li et al., 1998; Li & Oyama, 1998).

There is no evidence of catalytic O_3 decomposition on the glass or ash here as all samples show finite reactivity toward O_3, with surfaces saturating over the course of the experiments (e.g., Figure 1b). As observed for SO_2, reaction of the glass and ash with O_3 was irreversible on the timescale of our measurements, with neither desorption nor secondary uptake of O_3 measured upon stopping and restarting the gas flow. Determination of O_3/O_2 ratios by monitoring O_3 loss and O_2 evolution, i.e., to assess consistency with the expected overall stoichiometry of catalytic O_3 decomposition ($2O_{3(g)} \rightarrow 3O_{2(g)}$), was unfortunately hindered by the high O_2 background in the Knudsen reactor (see Text S5). It is possible that regeneration of reactive surface sites for O_3 uptake on the glass and ash was not observed within the measurement timescale due to slow formation of the O_2^{2-} intermediate and desorption of O_2 from these sites (Hanisch & Crowley, 2003; Li & Oyama, 1998). Alternatively, Karagulian and Rossi (2006) suggest that non-catalytic O_3 interaction with various mineral and dust substrates may proceed with irreversible O_3 adsorption forming a surface adduct without subsequently releasing O_2.

Ozone is a strong oxidizing agent which has been applied as a probe gas for reducing functional groups on various solid substrates (e.g., Setyan et al., 2010a, 2010b; Tapia et al., 2015, 2016), and we similarly attribute its uptake on the glass and ash material to adsorption on reducing surface sites (Maters et al., 2016). These sites may include oxygen deficiencies in the anionic oxide (O^{2-}) network at the solid-gas interface (Diebold, 2003) and transition metal atoms (e.g., Fe) in their lower valence state (e.g., Fe^{2+}) present in varying abundance on the aluminosilicate samples (Maters et al., 2016). Irreversible O_3 adsorption on such sites may involve insertion of an O or O_2 into an oxygen vacancy and/or interfacial Fenton-like chemistry, leading to formation of peroxide, superoxide, hydroxyl radical, and/or ferryl species at the surface (Enami et al., 2014; He et al., 2016; Li et al., 1998). Further research is necessary to elucidate the precise O_3 uptake mechanism on the glass and ash material studied here.

As shown by Maters et al. (2016), the typically lower N_i^{O3} values of the ash compared to the glass (Figure 3a and Table S4) conform with ash surfaces being relatively less reducing, likely due to exposure to an oxidizing mixture of hot gases and atmospheric air >600°C in the volcanic plume. The exceptional N_i^{O3} value displayed by Pinatubo ash, an order of magnitude higher than those of the other ash samples, may reflect a greater abundance of reducing surface sites provided by micrometric pyrite (FeS_2) in this ash (Maters et al. 2016). Notably, the γ_{O3} values of Pinatubo and Eyjafjallajökull ash were up to 6 times higher than those of the glass and other ash samples (Figure 3b and Table S4). This observation could also relate to the presence of FeS_2 in Pinatubo ash and Fe(II)-bearing saponite (general formula $Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$) in

Eyjafjallajökull ash (Paque et al., 2016), providing reducing surface sites for rapid uptake of O_3, although variation in γ values must be interpreted with caution and additional surface molecular/structural analyses would be needed to confirm this hypothesis.

4.3. Interaction Between Sulfur Dioxide and Ozone Uptake

For our glass samples, N_i^{O3} was consistently slightly higher after exposure to SO_2 (Figure 4a and Table S5), suggesting interaction of O_3 with adsorbed S species on glass surfaces. Previous studies of SO_2 uptake on mineral dust (e.g., Chinese loess and Saharan sand) and its component oxides (e.g., MgO, $CaCO_3$, Al_2O_3, Fe_2O_3, and SiO_2) have reported oxidation of chemisorbed SO_3^{2-}/HSO_3^{-} to SO_4^{2-}/HSO_4^{-} in the presence of an oxidizing agent (e.g., O_3, NO_2, and O_2 in air albeit more slowly) (Fu et al., 2007; Li et al., 2006; Ullerstam et al., 2002, 2003; Usher et al., 2002). Accordingly, basic sites reacting with SO_2 (forming adsorbed S(IV) species) on our glasses may be converted into reducing (oxidizable) sites (Ziolek et al., 1996), in addition to those already present, hence leading to detection of an increased abundance of reducing sites upon interaction with O_3. For the ash samples in contrast, there was no consistent difference in N_i^{O3} between the original versus the SO_2-exposed materials (Figure 4a and Table S5). This observation may be attributable to prior ash interaction with SO_2 in the volcanic plume/cloud; the presence of adsorbed S species already on "fresh" ash likely minimized an influence of additional SO_2 exposure (i.e., in the Knudsen flow reactor) on subsequent O_3 uptake by the ash. However, Pinatubo ash showed an exceptional fourfold decrease in N_i^{O3} following SO_2 exposure (Figure 4a), which may point to the existence of a poisoning effect of SO_2 on surface sites for O_3 adsorption on pyrite. Similarly, we note a sixfold decrease in γ_{O3} for the dacite glass after SO_2 exposure (Figure 4b), while no significant effect of SO_2 exposure on γ_{O3} for any of the other glass or ash samples is apparent. Further investigation is necessary to shed light on the factors underlying this observed heterogeneity in ash and glass surface reactivity.

Overall, we infer that SO_4^{2-}/HSO_4^{-} may be emplaced on sample surfaces at ambient temperature by adsorption of SO_2 gas (forming SO_3^{2-}/HSO_3^{-}) followed by interaction with O_3 gas (Li et al., 2006). This would be expected to occur on airborne ash since particles exposed to SO_2, coemitted during the eruption and present in the background atmosphere, are in contact with oxidizing agents from the moment of air entrainment in the volcanic plume/cloud. Sulfate is nearly ubiquitous on fresh ash surfaces (Witham et al., 2005) and has similarly been measured in aqueous leachates of the original ash samples studied here (Table S7). It is possible that this surface SO_4^{2-} derives in part from ash-gas interactions in the atmosphere in addition to ash-gas/condensate interactions during transit through distinct temperature-dependent reaction zones in the eruption plume/cloud (e.g., Ayris et al., 2013; Delmelle et al., 2007; Óskarsson, 1980; Rose, 1977; Taylor & Stoiber, 1973).

5. Implications and Conclusions

The reactive uptake of gaseous SO_2 and O_3 on ash and glass at ambient temperature, quantified here for the first time using a Knudsen flow reactor, likely involves SO_2 adsorption at basic sites and O_3 adsorption at reducing sites on the aluminosilicate surfaces. A lower SO_2 uptake on ash relative to glass is attributable to prior exposure of ash to acidic gases/condensates (including SO_2) within the eruption plume/cloud. Similarly, a generally lower O_3 uptake on ash compared to glass may relate to oxidation of ash surfaces in the high-temperature water-rich volcanic plume.

Irreversible uptake of SO_2 in the amount of 0.8 to 1 mg m^{-2} on glass powders has been reported by Schmauss and Keppler (2014), corresponding to 10 to 120 and 40 to 1600 times the N_i^{SO2} values obtained here for the glass and ash samples, respectively. However, those authors' measurements were acquired over hours at SO_2 partial pressures (>10 Pa) that would not be sustained for longer than minutes due to turbulent mixing of the volcanic plume/cloud with air (Sparks et al., 1997), and that greatly exceed the atmospherically representative SO_2 partial pressures used in the present study (<0.01 Pa). While our measurements suggest that partial saturation of ash surfaces in the volcanic plume/cloud may diminish ash reactivity toward SO_2 in the ambient atmosphere, the ranges of N_i^{SO2} and γ_{SO2} values exhibited by the glass and ash are comparable to those reported for oxide powders, mineral dust, and even liquid aerosols (Table S8).

Background O_3 depletion observed in some volcanic plumes/clouds is generally regarded as resulting from catalytic reaction with halogen radicals (Roberts et al., 2009; von Glasow, 2010). Using a γ_{O3} of 10^{-5} (taken as a value for mineral dust over its BET surface area), Vance et al. (2010) discounted heterogeneous reaction with ash as a viable O_3 loss mechanism. However, we measured a γ_{O3} range of 10^{-3} to 10^{-2} for volcanic ash over the geometric surface area initially probed by the gas, meaning that significantly less erupted ash than estimated by Vance et al. (2010) would be required to sustain heterogeneous O_3 removal consistent with the reductions observed in the field (see Text S6).

Based on our N_i^{O3} values, and assuming “light” or “intense” ash concentrations of 0.1 or 5 g m^{-3} in an ash plume/cloud (Marzano et al., 2010), we estimate that O_3 uptake on ash surfaces could deplete 0.1 to 4.6% or 4.6 to 230% of the background tropospheric O_3 concentration, respectively (see Text S7). These ranges are comparable to O_3 depletions attributed to destruction by volcanic halogen-derived reactive species (Surl et al., 2015; Vance et al., 2010). Interestingly, de Reus et al. (2000) measured a distinct anticorrelation between particle and O_3 concentrations in air parcels of a mineral dust plume. A similar effect may occur in the case of an ash plume/cloud since the ranges of N_i^{O3} and γ_{O3} values displayed by the glass and ash are comparable to those reported for oxide powders, mineral dust, and liquid aerosols (Table S9).

It remains to be verified whether ash surfaces can take part in catalytic decomposition of O_3 on timescales longer than those of our experiments, thereby increasing its removal from the atmosphere (Pittock, 1965). Remarkably, the ash samples show highly variable reactivities toward O_3, with uptake values of Pinatubo (N_i^{O3} and γ_{O3}) and Eyjafjallajökull (γ_{O3}) ash exceeding those of Tungurahua and Chaitén ash. These observations highlight a great heterogeneity in ash surface reactivity, implying that some eruptions may release ash particles with a strong potential for heterogeneous reaction with atmospheric O_3. Additional studies are needed to unravel what may control the variability and disparity in N_i^{O3} and γ_{O3} values of ash from different eruptions.

Our results also suggest that O_3 may facilitate oxidation of surface adsorbed S(IV) species, although more experiments are necessary to confirm this reaction. If so, SO_2 adsorption on ash surfaces in the cool volcanic cloud or atmosphere could generate additional reducing sites on the ash and thereby enhance its capacity to react with O_3. Moreover, this oxidation pathway (i.e., SO_3^{2-}/HSO_3^{-} to SO_4^{2-}/HSO_4^{-}) on ash surfaces would effectively minimize SO_2 desorption back into the gas phase (Adams et al., 2005), accordingly facilitating the role of ash as a sink for SO_2. In the atmosphere, adsorbed S(IV) species may be oxidized by O_2 as well via coupling with Fe^{3+} reduction to Fe^{2+} (Fu et al., 2007) in the aluminosilicate surfaces. While this mechanism likely prevails in the aqueous phase (Brandt & van Eldik, 1995), Fenton-like chemistry involving Fe^{3+}/Fe^{2+}-catalyzed redox chain reactions may take place at the solid-gas interface using strongly bound H_2O (He et al., 2016) and importantly could lead to regeneration of surface sites for atmospheric SO_2 withdrawal.

Overall, our study demonstrates that volcanic ash is reactive toward gaseous SO_2 and O_3 at ambient temperature and hence merits recognition as an atmospheric chemical agent alongside of volcanogenic gases/aerosols as well as mineral dust. We present benchmark experimental data on ash-gas reactivity which can also aid in improving quantification of heterogeneous reactions in atmospheric and climate models.

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