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Revision 2

Adsorption of sulfur dioxide on volcanic ashes

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ABSTRACT

The adsorption of pure sulfur dioxide gas on volcanic ashes has been studied from 0.1 mbar to 1 bar and from - 80 ˚C to + 150 ˚C. Finely ground synthetic glasses of andesitic, dacitic and rhyolitic composition served as proxies for fresh natural ash surfaces. Powders from two natural obsidian samples were also studied and yielded results broadly similar to the synthetic model systems. SO_2 adsorption on ash is partially irreversible; it appears that the first layer of SO_2 molecules absorbed on the surface cannot be removed. The pressure and temperature dependence of adsorption can be described by the equation $\ln c = A\, T^{-1} + B \ln p + C$, where c is the surface concentration of adsorbed SO_2 in mg/m^2, T is temperature in Kelvin and p is the partial pressure of SO_2 in mbar. A multiple regression analysis of the experimental data yielded A = 1645, B = 0.29, C = - 7.43 for andesite, A = 2140, B = 0.29, C = - 9.32 for dacite and A = 910, B = 0.21, C = - 4.48 for rhyolite. These data imply that adsorption strongly decreases with temperature, but only slowly decreases with decreasing partial pressure of SO_2. Therefore, adsorption primarily occurs in the cool and diluted parts of the volcanic plume. Model calculations show that most of the SO_2 may be removed from the plume, if the initial SO_2 concentration in the volcanic gases is low and the surface area of the ash is high. For high initial SO_2 concentrations, the fraction of SO_2 that is lost by adsorption decreases, since the amount of SO_2 in the gas phase is proportional to the SO_2 partial pressure p, while adsorption is proportional only to $p^{0.2} - p^{0.3}$. Adsorption of SO_2 on ash particles may therefore be one reason why the climatic impact of explosive volcanic eruptions does not always scale with total sulfur yield.

Keywords: sulfur dioxide, volcanic gases, ashes, adsorption

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INTRODUCTION

Volcanoes interact with the atmosphere in a variety of ways (McCormick et al. 1995; Mather 2008; Robock, 2000). During some explosive eruptions, sulfur dioxide is injected into the stratosphere, where it is photochemically oxidized to sulfate aerosols, which absorb sunlight and cool global surface temperatures (Bluth et al. 1993; McCormick et al 1995; Briffa et al. 1998; de Silva and Zielinski 1998; Robock 2000; Robock et al. 2009). Local ozone depletion may be related to halogens or to ash particles in the eruption plumes (McCormick et al. 1995; Textor et al. 2003; Rose et al. 2006). While ash particles probably have only a short-term effect on climate, their environmental impact is considerable. They may fertilize seawater (Frogner et al. 2001; Jones and Gislason 2008) or, depending on their composition, have toxic effects on vegetation, animals, and humans (Oskarsson 1980). In addition, ashes pose a severe hazard for aviation (e.g. Guffanti et al. 2010). Chemical interaction between ashes and gases in the eruption cloud is essential for understanding all of these phenomena. The surface of ashes is often highly enriched in sulfur and halogens, which is believed to be due to adsorption of HCl, HF and SO_2 (Rose 1977; Oskarsson 1980; Witham et al. 2005; Delmelle et al. 2007; Bagnato et al. 2013). Adsorption processes are important for the following reasons: (1) Adsorption of SO_2 and halogens on ashes will reduce the amount of climate-relevant gases delivered to the stratosphere, since ashes usually sediment within a few days back to the surface. (2) Adsorbed gas species and their reaction products are the main cause for the toxicity of ashes (e.g. Oskarsson 1980) and they may also contribute to the corrosion of aircraft engines. (3) Leachates of ashes are often used as a proxy for volcanic gas chemistry (Witham et al. 2005; Bagnato et al. 2011). However, a recent study by Bagnato et al. (2013) showed that the ratios of S, F, and Cl adsorbed on ashes of the 2010 Eyafjallajökull eruption are very different from the corresponding gas ratios measured in the plume. Therefore, the ratios of halogens and sulfur as determined from leachates can only be translated into gas compositions, if the adsorption isotherms, which relate the amount of absorbed gas to its partial pressure, are known. (4) Ash particles provide reactive surfaces in volcanic plumes that may catalyze various chemical reactions between gas species (e.g. Jordan et al. 2000). Adsorption of the surface of the particle is likely the first step in such a process.

Among volcanic gas species, sulfur compounds likely have the strongest environmental impact, as they are responsible for the formation of sulfate aerosols that may remain in the stratosphere for years. SO_2 is likely the most abundant sulfur species in plumes, with H_2S occurring only at very low oxygen fugacities; however, very oxidized arc magmas may release some of their sulfur directly in hexavalent form (likely as H_2SO_4 or sulfate; Binder and Keppler 2011; Ni and Keppler 2012). Unlike HCl, which is highly soluble in water and therefore easily removed by condensed water droplets, liquid films on particles or by ice (e.g. Textor et al. 2003), SO_2 is poorly soluble in water and adsorption on ashes may therefore be the main mechanism for depleting it from volcanic plumes after eruption. The change in plume SO_2 content has been directly observed in several recent eruptions, either by ground-based or satellite spectrometers; the data indicate that losses of 50 % or more within a few days are common, with loss rates varying widely (e.g. Rodriguez et al. 2008; Krotkov et al. 2010). In the stratosphere, SO_2 is ultimate converted into sulfate aerosols. The rate of this reaction, however, is limited by the low abundance of the OH radical, which is involved in the initial and rate-limiting step of the reaction chain. The characteristic time scale for the conversion of SO_2 to sulfate is in the order of tens of days, and even longer for high sulfur loading (Bekki 1995). Accordingly, this process cannot be responsible for any rapid loss of SO_2 from the cloud.

Experimental data on the interaction of SO_2 with the surface of ash particles are very limited. Ayris et al. (2013) studied the interaction of tephra with SO_2 and suggested that sulfur may be removed from the gas phase by the diffusion of Ca^{2+} to the surface of the glass particles followed by the precipitation of $CaSO_4$. As the diffusion of Ca^{2+} is strongly temperature dependent, this process may only occur at high-temperature, near vent conditions or inside the vent. Indeed, Ayris et al. (2013) conclude that this scavenging mechanism is only significant if fragmentation of the magma occurs more than 500 meters below the surface. However, the study of Bagnato et al. (2013) showed a major increase of adsorbed sulfur with distance from the vent for the 2010 Eyjafjallajökull eruption, which suggest that most of the sulfur scavenging occurs at rather low temperatures in the volcanic plume at high altitude. The interaction between SO_2 and ashes under these low-temperature conditions is hardly studied (Gu et al., 1999). We therefore present here a systematic experimental study of SO_2 adsorption on volcanic ashes, from – 80 ˚C to + 150 ˚C, and from 0.1 mbar to 1 bar

SO_2 pressure. Our study therefore covers most of the temperature and SO_2 partial pressure range that is expected for the cool, dilute parts of a volcanic plume (e.g. Textor et al. 2003, 2006). As a proxy of fresh, unweathered volcanic ash we used fine powders of both synthetic and natural silicate glasses. While ash is a mixture of various materials, including fine rock fragments, crystals and glasses, it is likely that fresh amorphous glass surfaces with their high defect population are the preferred sites of adsorption (e.g. Rendulic 1988; Leed and Pantano 2003). In particular for explosive, intermediate to silicic eruptions, glassy material is usually the dominant constituent of fresh ash.

EXPERIMENTAL METHODS

Sample preparation

Fe-free andesite, dacite and rhyolite glasses were prepared from mixtures of high-purity (> 99.9 wt. %) SiO_2, $Al(OH)_3$, $Mg(OH)_2$, $CaCO_3$, Na_2CO_3, and K_2CO_3. They were mixed in a planetary mill under ethanol and then slowly heated in a platinum crucible to 1100 ˚C for decarbonation and dehydation. The charges were then melted at 1600 ˚C in a high temperature furnace for 2 hours and quenched in water. The glasses produced contained some bubbles, but were free of crystals. Chemical compositions are given in Table 1. The glasses were then ground in a planetary mill for 5 – 10 min without adding any liquid, to avoid adsorption on the fresh surfaces. The surface area of the powders was determined using a Micrometrics Gemini III 2375 surface analyzer by measuring the BET adsorption isotherm of nitrogen (Brunauer et al. 1938). Surface areas obtained were in the range of 2600 – 4500 m^2/kg, which implies an average grain size in the order of 0.6 – 1 μm. This is comparable to the low grain-size fraction of natural ashes (e.g. Carey and Sigurdsson 1982). For some experiments, natural obsidian glasses from Lipari (Aeolian Islands, Italy; rhyolitic composition) and from Puu Waawaa (Hawaii; trachytic composition) were ground up to fine powders in the same way as the synthetic samples. The synthetic samples were chosen to be iron-free to avoid complications arising from possible redox reactions between ferric iron and SO_2; the natural glasses were studied

to test whether the adsorption isotherms measured for the synthetic samples are comparable to those of natural compositions.

Adsorption and desorption experiments

Adsorption and desorption measurements were carried out in a glass apparatus shown in Fig. 1. Pressure in the apparatus was measured by a Vacuubrand DVR 5 vacuum gauge with an Al_2O_3-coated pressure transducer that is inert to SO_2. The pressure transducer is a plate capacitor, which transforms mechanical deformation due to external pressure into a change of capacity. The instrument has a measurement range of 0.1 mbar to 1 bar, with an accuracy of ± 0.1 mbar up to 10 mbar and ± 1 mbar up to 1 bar.

At the beginning of an experiment 30 – 50 g of finely ground glass powder was placed in the sample tube and the entire system was evacuated to < 0.1 mbar for several hours with a rotary vane pump (Vacuubrand RZ6). A liquid nitrogen-cooled cold trap was placed between the pump and the apparatus in order to avoid contamination of the sample by oil fumes and to protect the pump from any gases released from the samples. After switching off the vacuum pump, the pressure in the system was observed for several hours to check for leaks. Only if pressure remained at < 0.1 mbar, the experiment was continued. After this, the valve to the sample was closed and the round flask was filled with a desired pressure of SO_2 from the gas bottle. The two washing flasks filled with paraffin as shown in Fig. 1 served as a safety valve to avoid any overpressure inside the glass apparatus. When the valve connecting the sample with the gas reservoir was opened, first a small, instantaneous pressure drop occurred because of the increase in available gas volume. This was followed by a continuous decrease in pressure due to absorption of SO_2 on the ash surface. Most of the decrease occurred rapidly within the first 10 – 30 minutes. After a few hours, pressure kept decreasing only very slightly and after one or two days, it remained constant, indicating that equilibrium between gas and ash surface had been reached. We carried out some long-time experiments with durations up to two weeks; they showed no further change of pressure in the system. From the value of equilibrium pressure achieved after one or two days and its difference to the original pressure, the amount of adsorbed SO_2 can be calculated.

A measurement cycle always started with adsorption at low pressure. After equilibrium had been reached, the valve to the sample was closed and a higher pressure of gas was filled into the reservoir and the absorption experiment was repeated. Several adsorption experiments were carried out in steps until a final pressure near 1 bar was reached. After this, the valve between sample and reservoir was closed and the pressure of SO_2 in the round flask was reduced by means of the rotary vane pump. After opening the valve between sample and reservoir, first a slight increase in pressure occurred because of the higher gas pressure in the sample tube, followed by a continuous increase in pressure due to desorption of SO_2 from the ash surface. Again, after a few hours, a steady state indicating equilibrium was reached. The desorption step was then repeated several times with decreasing pressures, until nearly zero mbar were reached. Experiments at variable temperature were carried out by immersing the sample container in an oil bath or in a cooling mixture.

In order to quantify adsorption, three volumes in the system need to be known precisely: V_1, the volume of the gas reservoir (round glass flask plus glass tubing attached to it), V_2, the volume of the empty sample tube and V_3, the empty gas space in the sample tube after filling it with glass powder. V_2 was first determined by filling the sample tube completely with water and weighing it. This yielded V_2 = 19.00 ml ± 0.3 ml. V_1 was measured by determining by filling the gas reservoir first with air and then connecting it to the evacuated sample tube. From the initial pressure p_1 in the reservoir and the final pressure p_2 one can calculate V_1 by applying the ideal gas law pV = nRT (with p = pressure, V = Volume, n = number of mols, R = gas constant, and T = temperature) : $V_1 = \frac{p_2 V_2}{p_1 - p_2}$. This yielded V_1 = 617ml ± 6 ml. The free gas volume V_3 in the sample container can be calculated by subtracting the volume of the glass powder from V_2: $V_3 = V_2 - \frac{m_{glass}}{\rho_{glass}}$, where m_{glass} and ρ_{glass} are mass and density of the glass powder, respectively. The pressure drop Δp due to adsorption can be readily converted into the number of adsorbed moles Δn, if the ideal gas law is applied:

$$\Delta n = \Delta p \frac{V_1 + V_3}{RT}.$$

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However, while the ideal gas law describes air at 1 bar and lower pressures very well, for SO_2 significant deviations may occur due to non-ideal behavior. Therefore, all calculations for SO_2 were carried out using the van der Waals equation

$$p = \frac{nRT}{V - b} - \frac{an^2}{V^2}$$

with the constants a = 0.69 Pa m^6mol^{-2} and b = $5.7 \cdot 10^{-5}$ m^3mol^{-1} for SO_2. In order to calculate the number of absorbed moles of gas from the observed pressure drop, the van der Waals equation was rearranged into a third-order equation in n, which was solved by the Cardano formula. At room temperature and above, the differences between the calculations using ideal gas law and the van der Waals equation are negligible. However, they may amount to a few percent (relative) at 0 ˚C and below. The van der Waals equation was chosen, because it is well suited to describe non-ideal gases at low pressures. However, as the deviations from ideal gas behavior are small under all conditions studied, very similar results could also have been obtained, e.g. by a virial type equation.

Uncertainties in the calculated surface concentrations were determined by a full error propagation analysis including the uncertainties of all parameters that enter the calculation. Main sources of uncertainty are the pressures, the volumes in the system and the specific surfaces of the powders.

EXPERIMENTAL RESULTS

Adsorption experiments at room temperature

Adsorption and desorption isotherms for rhyolite, dacite and andesite glass powders are shown in Fig. 2. The shape of the curve for adsorption, most clearly seen for the dacite sample, corresponds to a “type II” isotherm according to the classification of Brunauer (1945): The amount of adsorbed gas first increases steeply, then reaches a nearly flat plateau until it starts to increase again. This type of curve suggests that adsorption occurs in several layers. The nearly flat part of the curve corresponds

232 approximately to the adsorption of the first layer of gas molecules on the surface.
233 When pressure is reduced, desorption occurs. However, desorption is not fully
234 reversible; rather, some hysteresis-like behavior is obvious from Fig. 2, implying that
235 during adsorption and/or desorption, only some metastable equilibrium is reached.
236 The amount of SO_2 remaining on the surface at very low pressure corresponds
237 approximately to the first layer of gas molecules on the surface, i.e. to the amount of
238 SO_2 adsorbed in the shallow part of the adsorption curve as seen in Fig. 2. In order to
239 confirm that some SO_2 remains irreversibly attached to the surface, the samples were
240 analyzed by X-ray fluorescence (XRF) after the end of the desorption experiment.
241 Bulk SO_2 concentrations of 2381 ± 328 ppm by weight were observed for the rhyolite
242 sample, 1286 ± 97 ppm for the dacite sample and 783 ± 33 ppm for the andesite
243 sample. These values are broadly consistent with the data obtained from the
244 adsorption/desorption data (Table 2). The differences may be related to the handling
245 of the samples in air of about 50 % relative humidity during preparation for XRF
246 analysis, which may have caused some desorption of SO_2 by interaction with air or
247 water vapor. The generally quite high bulk sulfur contents of these samples reflect
248 their small grain size and correspondingly high specific surface. The oxidation state of
249 sulfur on the surfaces of andesite, dacite, and rhyolite glasses exposed to SO_2 gas for
250 24 hours was studied by Farges et al. (2009). From sulfur K-edge XANES data, it
251 appears that most of the sulfur is adsorbed as sulfate, which may have formed by
252 reaction of SO_2 with broken bonds at the glass surface.
253
254 **Adsorption experiments at variable temperature**
255 Adsorption isotherms of SO_2 on rhyolite glass powder are shown in Fig. 3a for
256 variable temperatures, ranging from - 80 ˚C to + 150˚C. Clearly adsorption strongly
257 decreases with temperature. As sulfur dioxide condenses to a liquid already at -10 ˚C
258 at 1 bar, the low-temperature adsorption experiments could only be carried out up to
259 low pressures. Adsorption measurements on andesite and dacite glass at 0˚C and 20˚C
260 show a similar increase of adsorption with decreasing temperature as seen for rhyolite
261 (Fig. 3b, c). The decrease of adsorption with increasing temperature is typical for the
262 interaction of gases with surfaces. Since the entropy of SO_2 in the gas phase is higher
263 than on a surface and since the entropy contribution $T\Delta S$ to Gibbs free energy ΔG =

264 ΔH –TΔS (where ΔH is the adsorption enthalpy) increases with temperature, high
265 temperatures shift the equilibrium towards the free gas.
266
267 Measured adsorption data at different temperatures were fitted to BET (Brunauer-
268 Emmet-Teller) adsorption isotherms, which are designed to describe multilayer
269 adsorption (Brunauer et al. 1938):
270
271 $$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{p}{p_0}\right)$$
272
273 where p is pressure, V is the volume of the adsorbed gas at STP (standard pressure
274 and temperature), p_0 is the condensation pressure of the gas at the given temperature,
275 V_m is the monolayer capacity, i.e. the volume of gas adsorbed in the first complete
276 layer of gas molecules, where the volume is given at STP conditions, and C is a
277 constant related to the interaction energy between gas molecules and surface. This
278 equation implies that a plot of $\frac{p}{V(p_0 - p)}$ versus $\frac{p}{p_0}$ should yield a straight line with
279 intercept $\frac{1}{V_m C}$ and slope $\frac{C-1}{V_m C}$, which allows the two constants V_m and C to be
280 determined. Bet isotherm plots for rhyolite, dacite and andesite composition at 0˚C
281 and 25˚C are shown in Fig. 4, the corresponding BET constants are compiled in Table
282 3.
283
284 **Adsorption experiments with natural obsidian glasses**
285 Figure 5 shows adsorption and desorption isotherms measured on powders of natural
286 obsidians from Lipari (Aeolian Islands, Italy; rhyolitic composition) and from Puu
287 Waawaa (Hawaii; trachytic composition) at 0 ˚C. The data are broadly comparable to
288 those for the synthetic samples (Fig. 3), suggesting that the presence or absence of
289 iron (1.5 wt. % FeO_{tot} for Lipari obsidian and 4.1 wt. % for Puu Waaawaa obsidian)
290 does not fundamentally change the absorption behavior. BET constants derived from
291 these data are also included in Table 3.
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A multiple regression model of SO_2 adsorption

In order to construct a numerical model for SO_2 adsorption that includes both partial pressure and temperature, the data for each glass composition were fitted to an equation

$$\ln c = A\frac{1}{T} + B \ln p + C$$

where c is the amount of adsorbed SO_2 in mg/m^2 (milligram per m^2 of surface area), p is SO_2 partial pressure in mbar and T is temperature in Kelvin; A, B, and C are constants obtained by multiple regression. This equation corresponds to a Freundlich adsorption isotherm (Freundlich, 1907) with an added term AT^{-1} to describe the temperature dependence. The Freundlich isotherm is an empirical equation, which often describes absorption equilibria well; because of its functional simplicity, it is particularly suitable to fit absorption data over a wide range of P and T conditions. The constant A is related to the adsorption enthalpy ΔH by $A = -\Delta H/R$ where R is the gas constant. Fit parameters for this equation are given in Table 4; Figure 6 compares predicted and observed surface concentrations of SO_2. The calculated values for the coefficient A correspond to adsorption enthalpies ΔH (in kJ/mol) of $– 7.6 \pm 1.0$ for rhyolite glass, $- 17.8 \pm 3.1$ for dacite glass, and $– 13.7 \pm 3.0$ for andesite glass. The value for dacite glass is close to the - 26 kJ/mol reported for SO_2 adsorption on MCM-41, a mesoporous alumosilicate material, at high surface coverage (Branton et al. 1995).

SULFUR ADSORPTION IN VOLCANIC PLUMES

Based on ash leachate data of from the 1974 Fuego eruption, Rose (1977) already suggested that about 33 % of the originally released sulfur was scavenged by ash. With the quantitative adsorption data provided in this study, it is now possible to quantify the extent of SO_2 scavenging by ashes and its dependence on eruption parameters. In this context, the most important results of this study are:

(1) SO_2 adsorption strongly decreases with temperature; therefore, probably most of the adsorption occurs in the cold parts of the plume higher in the atmosphere, while adsorption at magmatic temperatures is likely of minor importance. The short

residence time of particles at near-vent conditions in explosive eruptions (a few minutes at most) as opposed to the long residence time in the umbrella part of a plume (hours to days) also suggest that most adsorption must occur at low temperature. This is entirely consistent with the observation by Bagnato et al. (2013) that the sulfur load on ash surfaces of the 2010 Eyafjallajökull eruption increased by more than a factor of three with increasing residence time and distance from the vent.

(2) The coefficient B in the multiple regression equations (Table 4) suggest that SO_2 adsorption increases only slightly with the partial pressure of SO_2, i.e. with $p^{0.2}$ to $p^{0.3}$. In other words, SO_2 adsorption remains strong at very low partial pressures, again confirming that adsorption occurs mostly in the dilute and cold parts of plumes. Moreover, while the amount of adsorbed SO_2 increases only with $p^{0.2}$ - $p^{0.3}$, the amount of SO_2 remaining in the gas phase is directly proportional to the SO_2 partial pressure p. Therefore, the fraction of total SO_2 that is not adsorbed must increase with $p/p^{0.3} = p^{3.3}$ or $p/p^{0.2} = p^5$. This means that the initial SO_2 partial pressure, i.e. the molar fraction of SO_2 in the volcanic gases exerts a major control on the extent of SO_2 adsorption, together with the ratio of ash surface to total gas volume.

(3) The first monolayer of SO_2 on ash surfaces appears to be irreversibly adsorbed, implying that this part of SO_2 is permanently removed from the plume. SO_2 that is adsorbed in multiple layers may be released again during desorption, when the SO_2 partial pressure is reduced, e.g. upon dilution of the plume by entrainment of air. The data in Fig. 2 suggest that the amount of SO_2 that may be irreversibly adsorbed on ash surfaces is close to 0.8 to 1 mg/m^2. Interestingly, the data of Bagnato et al. (2013; their Fig. 15c) suggest that at residence times of ashes in the plume of 1 hour and above, sulfur concentrations on the ashes level out at 1.2 mg/m^2 of sulfate, which converts to 0.9 mg/m^2 of SO_2, in very good agreement with the experimental data reported here.

(4) Glass composition has only a relatively minor effect on the extent of SO_2 adsorption on ash surfaces. The differences between the data for rhyolite, dacite and andesite glass (Fig. 2) are mostly below 25 % (relative), which is negligible compared to the much stronger effects of pressure and temperature (Fig. 3.).

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The experimental data presented here were all obtained by equilibrating ash surfaces with pure SO_2 gas, while in nature, the gas phase will be a mixture of volcanic gases and air. The main component of the volcanic gases is usually H_2O, followed by CO_2, SO_2 and HCl. SO_2 is typically in the range of up to a few mole %, with HCl usually being somewhat less abundant (Symonds et al. 1996). In the cold parts of a volcanic plume, these gases are highly diluted by mixing with air, which reduces potential interactions between the gases by competition for adsorption sites. In particular for HCl, the concentration in the plume is strongly reduced, due to the high solubility of HCl in liquid water and its incorporation into ice (Textor et al. 2003; Rose et al. 2006). Because of the very low HCl partial pressures resulting, interaction between HCl and SO_2 in the adsorption process on ashes can likely be ignored. Water vapor, however, will be much more abundant than SO_2, both in the initial volcanic gases and in the diluted plume. This will even be so for initially CO_2-rich volcanic gases, because of the extensive mixing with (humid) air (see the discussion of dilution factors below). During the preparation of the samples used in this study, direct contact with liquid water during grinding was avoided, as this would very likely have caused some change in surface properties due to leaching. However, the powder samples were handled in air of average humidity and several studies have shown that any silicate surface exposed to air of normal humidity will immediately be coated by water molecules, which will not be removed even in vacuum, unless the sample is heated to temperatures far above 100 ˚C (Kunkel 1950; Nelson and Vey 1968; Zhuravlev 1987; Garofalini 1990; see also Keppler and Rauch 2000; Lathem et al. 2011). Measurement of the adsorption of water vapor on silicate glass (Razouk and Salem 1948) show that it can be described by a type II isotherm, very similar in shape to those measured for SO_2 in this study. Already at relative humidities of < 10 %, the surface of the glass is nearly completely covered by water molecules and the isotherm remains nearly flat (i.e. not much additional adsorption occurs) up to very high relative humidities of > 70 %. Therefore, the samples investigated in this study likely had surfaces initially coated by water molecules and the adsorption measurements are entirely realistic for the processes that occur in dilute volcanic plumes at high altitude.

To illustrate the effect of ashes on the SO_2 yield of explosive eruptions, we use our data to simulate the behavior of SO_2 in a plume. For quantitative calculations, the following factors have to be considered:

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(1) Available ash surface. The 1980 Mt. St Helens eruption produced ash with a median grain size around 10 μm (Carey and Sigurdsson 1982; Genarau et al. 2012). Assuming a uniform grain size of 10 μm, a cubic shape of individual grains and a density of 2.4 g/cm^3, yields a specific surface of the ash of 250 m^2/kg. This is quite comparable to specific ash surfaces measured for the 2010 Eyafjallajökull eruption (Bagnato et al. 2013). For comparison, we will also discuss the situation for ashes with a grain size of 1 μm, and a specific surface of 2500 m^2/kg, similar to the powders used in our experiments. While this size appears small compared to measured grain size distributions of ashes, it has to be kept in mind that these measurements are usually carried out on ashes that have sedimented out of the plume within a few hours or days. The grain size of ash deposits often decreases exponentially with distance from the vent. Very fine particles will remain in the plume for longer times and may therefore be under-represented in the sampling (Pyle 1989, Bonadonna and Houghton 2005). Using satellite data, Wen and Rose (1994) estimated an average particle size of 2 – 2.5 μm in the ash cloud of the 1992 eruption of Crater Peak/Spurr Volcano. This would be similar for the finest grain sizes used in our experiments. On the other hand, Bonadonna et al. (2011) report a median near 250 μm for the total grain size distribution of the 2010 Eyafjallajökull eruption, with a fine-ash content of 30 wt. %. Note, however, that the fine ash particles contribute much more strongly to the average specific surface than large particles and therefore, the specific surface of the ash will be mostly determined by the abundance of very fine particles.

(2) Temperature. Many plumes from explosive eruptions reach the stratosphere and spread there horizontally. Due to extensive mixing with air and conductive heat loss, the temperature of the plume gases will be similar to the ambient temperature (e.g. Sparks 1997; Textor et al. 2003, 2006), which is approximately 220 K (-53 ˚C) at 10 km altitude. We will assume this temperature for all our calculations.

(3) Mass ratio of sulfur dioxide to ash. This ratio is determined by the composition of the volcanic gases and by the mass ratio of gas to ash. Measured SO_2 contents in volcanic gases vary widely, between < 1 mole % to > 10 mole % (Symonds et al. 1994), where 1 mole % corresponds to 3.47 wt. % in a gas phase consisting mostly of

water vapor. This wide variation may partially be due to the strong partitioning of SO_2 into the vapor phase in equilibrium with a silicate melt (e.g. Keppler 2010 and references therein), implying that SO_2 will be highly enriched in the initial fluids released at the beginning of an eruption and depleted during further degasing. For the 1991 Mt. Pinatubo eruption, an SO_2 concentration in the pre-eruptive fluid phase between 0.56 and 0.85 wt. % was estimated (Keppler 1999), i.e. the gas released by this eruption was not particularly sulfur-rich, but the mass ratio of pre-eruptive fluid to magma (0.08 – 0.25; Keppler 1999) was very high. For the weight ratio of total volcanic gases to (glassy) ash we will here assume a value of 0.05, i.e. the mass of the gases released is 5 % of the mass of the magma. This assumption is in line with the pre-eruptive volatile (mostly water) contents of mafic arc magmas, which usually cluster between 2 and 6 wt. % (Métrich and Wallace, 2008; Plank et al. 2013); somewhat higher volatile concentrations may be reached in more evolved magmas.

(4) Partial pressure of SO_2 in the plume. Compared to the partial pressure in the initial volcanic gases, the partial pressure in the plume will be reduced by the decrease of ambient pressure and by the mixing with air. At an elevation of 10 km, ambient pressure decreases from about 1 bar near sea level to about 200 mbar. This effect alone would therefore reduce the partial pressure of 1 mole % SO_2 in a volcanic gas from 10 mbar to 2 mbar, assuming ideal gas behavior, which is a very good approximation at these low pressures. The degree of mixing with air depends on various physical parameters of the eruption. We will assume a dilution of the volcanic gas by air by a factor of 100:1 in our calculations, which is a plausible value for a range of parameters (initial temperatures around 1000 K, entrainment coefficients ε around 0.09 and a weight ratio of volcanic gases to ash of 0.05; for discussion, see Sparks et al. 1997; Schmauss-Schreiner 2007). In the given example, this will reduce the SO_2 partial pressure to 0.02 mbar. We note, however, that the extent of adsorption is rather insensitive to this parameter, as absorption only increases with $p^{0.2}$ - $p^{0.3}$. Therefore, increasing the dilution factor of the plume from 100 to 1000 would only reduce the amount of adsorbed SO_2 by a factor of 1.5 – 2.

If one assumes a specific surface of the volcanic ash of 250 m^2/kg, a mass ratio of gas/ash of 0.05 as discussed above and 1 mole % of SO_2 in the gas, complete

462 adsorption of SO_2 on the ash surface would yield a surface concentration of 6.94
463 mg/m^2. A comparison with the data in Figure 2c and 3 shows that this values is at
464 least three times higher than the highest surface concentration measured, even at very
465 high SO_2 partial pressures which likely will never be reached in a plume. Therefore,
466 even under the most favorable circumstances, not more than about 30 % of the total
467 SO_2 in the plume could be absorbed by ash, the real fraction likely being lower. This
468 fraction will decrease further, if the initial SO_2 concentration in the volcanic gas is
469 higher than 1 mol %, because the amount of absorbed SO_2 only increases with $p^{0.2} - p$
470 $^{0.3}$. On the other hand, if one assumes a specific surface of the ash of 2500 m^2/kg, at 1
471 mol % of SO_2 in the gas, total absorption would lead to a surface concentration of
472 0.69 mg/m^2, which is well in the range of values that may be achieved at very low
473 partial pressures of SO_2 (Fig. 2 and 3), so that removal of most of the SO_2 from the
474 plume may be possible. Already these simple considerations show that (1) nearly
475 complete loss of SO_2 from a plume by adsorption may be possible, if the initial SO_2
476 concentration is far below 1 mole % and /or the ash is very fine-grained; (2) for initial
477 SO_2 concentrations of 1 mole % or higher, most of the SO_2 will likely remain in the
478 gas phase of the plume.
479
480 For a quantitative modeling of SO_2 adsorption, the adsorption isotherm at plume
481 temperatures (220 K) has to be calculated from the fit parameters in Table 4. This
482 isotherm is shown in Figure 7 for andesite glass. For 1 mole % SO_2 in the volcanic
483 gas, the SO_2 partial pressure in the plume before adsorption will be 0.02 mbar. For
484 andesite glass with a very large surface (specific surface 2500 m^2/kg, mass ratio
485 gas/ash = 0.05), this partial pressure corresponds to a surface concentration of SO_2 of
486 0.34 mg/m^2. However, this is not the equilibrium surface concentration, because the
487 SO_2 partial pressure in the gas decreases as SO_2 is being absorbed. The equilibrium
488 surface concentration for a given initial SO_2 partial pressure can be obtained by a
489 graphical method (Fig. 7). The initial state of the system corresponds to a surface
490 concentration of SO_2 of zero and a SO_2 partial pressure of 0.02 mbar. This state is
491 marked as point A in Figure 7. Total absorption of all SO_2 (resulting in zero partial
492 pressure) would lead to a surface concentration of 0.69 mg/m^2; this is point B in Fig.
493 7. As absorption proceeds, the increase in surface concentrations has to be
494 proportional to the decrease in partial pressure of SO_2, as both quantities are
495 proportional to the numbers of absorbed moles of SO_2. Therefore, in the diagram

shown in Figure 7, the system has to move along a straight line from point A in the direction towards point B during the adsorption process, until adsorption stops because equilibrium is reached. This point is given by the intersection of the straight line with the adsorption isotherm, which relates the surface concentration to the SO_2 partial pressure in equilibrium. In the present example, the surface concentration is 0.29 mg/m^2, with an equilibrium SO_2 partial pressure of 0.012 mbar. This implies that 42 % of the SO_2 initially released by the eruption was scavenged by ash. The latter number is obtained as the ratio of the equilibrium surface concentration to the (hypothetical) surface concentration corresponding to total absorption (0.69 mg/m^2). This percentage can also be obtained graphically; in Figure 7, it is the ratio of the distance between the equilibrium point and point A to the distance between A and B.

Figure 8 shows model calculations for the fraction of SO_2 in a plume adsorbed on ashes, for two different specific ash surfaces and for variable SO_2 contents in the volcanic gas. Obviously, SO_2 absorption can be very important if the ash surface is high and if the initial SO_2 content of the volcanic gas is below 1 mole %. All calculations were carried out for a mass ratio of volcanic gas to ash of 0.05. However, the result of the calculations does not change, if the product of the mole fraction of SO_2 in the volcanic gas and the mass ratio of gas/ash remains constant. In other words, for a gas/ash mass ratio of 0.1 and an SO_2 content of 1 mole %, the fraction of SO_2 adsorbed on ash is the same as for a gas/ash mass ratio of 0.05 and 2 mole % SO_2.

Our data give first insights into the initial adsorption processes occurring in volcanic plumes at high altitude. Subsequent to the adsorption of SO_2 and other gases on ash particles, surface reactions may occur that involve the leaching of cations out of the ash and the re-precipitation of salts on the ash surface (e.g. Delmelle et al. 2007; Bagnato et al. 2013). Very likely, however, these processes require the presence of liquid water and therefore, they only occur when ash particles started to sediment down to warmer parts of the atmosphere.

According to the results presented here, adsorption may under some circumstances strongly affect the sulfur yield of eruptions and by implication, their impact on climate. Clearly, both the relative amount of available ash surface (as controlled by

the gas mass fraction and the grain size or specific surface of the ash) and the initial SO_2 concentration in the gases are critical parameters. If SO_2 is very diluted, e.g. by water vapor in the volcanic gas, it may be largely adsorbed by the volcanic ash and the environmental impact of such an eruption is like to be small. On the other hand if the initial SO_2 concentration in the volcanic gas, or the ratio of volcanic gas to ash is high, only a much smaller fraction of SO_2 will be adsorbed and a much stronger impact on climate is to be expected. The 1991 Mt. Pinatubo eruption may have been such a case; Guo at al. (2004) used infrared remote sensing data from satellites to infer that the cloud initially contained 50 Mt of ash particles, but up to 12 Mt of SO_2. From the data presented in this study, it is clear that sulfur scavenging by ash is insignificant under such circumstances.

If one compares two eruptions that release the same total amount of SO_2, the one releasing more water vapor will be more explosive. However, the dilution of SO_2 by water vapor will also enhance adsorption of SO_2 on ash and therefore, the more explosive eruption may have a smaller impact on climate. This effect is further enhanced by the stronger fragmentation and therefore larger ash surface resulting from a more explosive eruption. SO_2 adsorption on ashes may therefore be a decisive factor in controlling the environmental impact of volcanic eruptions. In particular, it may be one of the reasons why atmospheric cooling does not always correlate with the magnitude of an eruption or with total sulfur yield.

IMPLICATIONS

The model for SO_2 adsorption described here allows the scavenging effect of volcanic ashes on the SO_2 abundance in volcanic plumes to be fully quantified, such that this effect can now be incorporated in numerical models of plume chemistry. The example calculations shown in this paper cannot explore the full range of parameters that may occur in plumes. However, they suggest that the relative amount of available ash surface and the initial concentration of SO_2 in the volcanic gases are the most important parameters in controlling the extent of adsorption. If the initial SO_2 concentration is low (< 1 mole %) and the specific surface area of the ash is high, most of the SO_2 may be adsorbed. This is because adsorption only increases with $p^{0.2}$ – $p^{0.3}$, where p is SO_2 partial pressure and therefore, the fraction of SO_2 in the plume

564 that is not adsorbed on ash must increase with $p^{3.3}$ to p^5. As SO_2 adsorption on
565 volcanic ash may under some circumstances greatly reduce the effect of volcanic
566 eruptions on climate, the model presented in this study should allow a significant
567 improvement in forecasting the environmental impact of volcanic eruptions.
568
569
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576
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Table 1. Bulk chemical composition (in wt. %) and density (in g/cm^3) of synthetic glasses

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Density
Andesite	56.42	20.81	7.07	7.05	3.68	1.74	2.34
Dacite	67.52	16.25	5.24	2.78	4.29	3.16	2.63
Rhyolite	77.21	12.13	3.08	0.72	2.80	3.46	2.36

Notes: Chemical composition from XRF, density from pycnometer measurements

Table 2. Amount of SO_2 adsorbed on glass powders at 1 bar and amount of SO_2 remaining on the glass surface after desorption. All data for 25 ˚C.

	Adsorbed SO_2		Pressure
	in mg/m^2	in wt.%	mbar
Rhyolite	1.64 ± 0.32	0.39 ± 0.04	940
Dacite	1.30 ± 0.18	0.41 ± 0.03	968
Andesite	1.30 ± 0.22	0.34 ± 0.03	965
	SO_2 after desorption		Pressure
	in mg/m^2	in wt.%	mbar
Rhyolite	0.94 ± 0.23	0.22 ± 0.05	6.8
Dacite	0.63 ± 0.16	0.19 ± 0.04	0.9
Andesite	0.75 ± 0.23	0.19 ± 0.04	0.1

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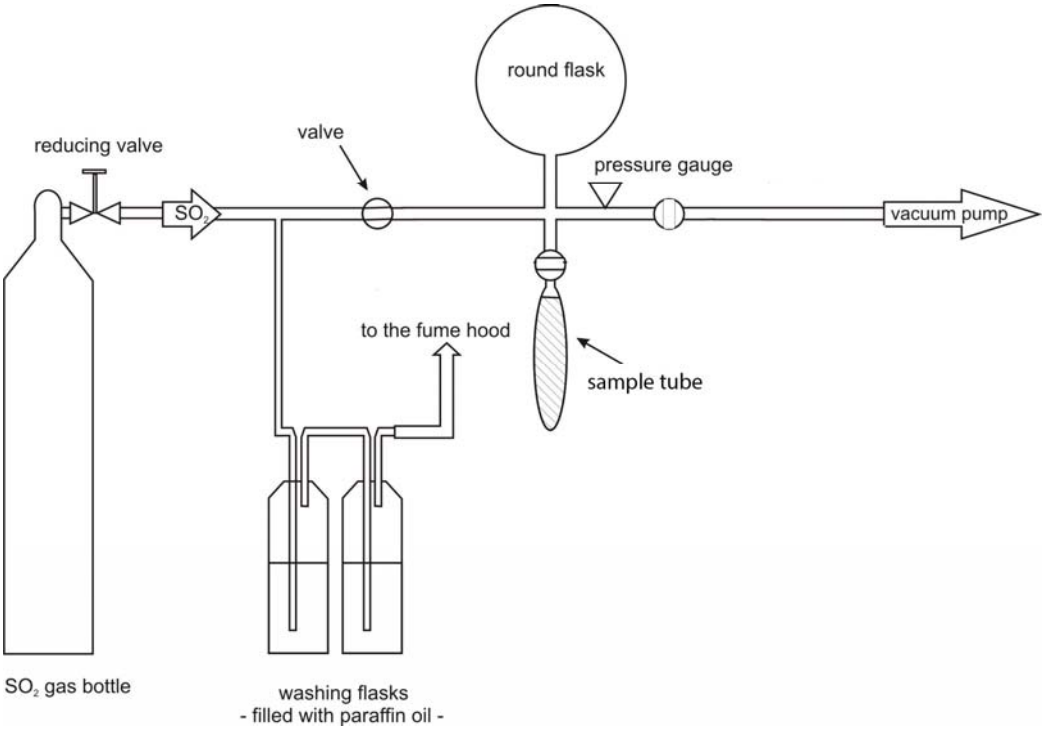
Table 3. BET fit parameters for the adsorption of SO_2 on glasses.

	T in ˚C	C	V_m in cm^3/m^2	R^2
Rhyolite	25	13.1 ± 3.0	0.40 ± 0.08	0.86
	0	93.4 ± 4.7	0.32 ± 0.06	0.99
Dacite	25	19.6 ± 1.0	0.29 ± 0.03	0.97
	0	65.9 ± 3.3	0.34 ± 0.04	0.98
Andesite	25	14.8 ± 3.8	0.40 ± 0.07	0.82
	0	72.0 ± 3.6	0.29 ± 0.05	0.99
Lipari obsidian	0	16.00 ± 0.8	0.33 ± 0.02	0.99
Puu Waawaa obsidian	0	20.10 ± 1.0	0.47 ± 0.02	0.98

Table 4. Multiple regression coefficients for SO_2 adsorption on rhyolite, dacite and andesite glasses. Data were fitted to the equation $\ln c = A/T + B\ln p + C$, where c is the surface concentration of adsorbed SO_2 in mg/m^2, p is SO_2 partial pressure in mbar and T is temperature in Kelvin.

	A	B	C	R^2	Error in ln c
Andesite	1645 ± 363	0.29 ± 0.02	-7.43 ± 1.33	0.92	0.22
Dacite	2140 ± 379	0.29 ± 0.02	-9.32 ± 1.41	0.91	0.20
Rhyolite	910 ± 124	0.21 ± 0.03	-4.48 ± 0.49	0.75	0.37



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767 **FIGURE 1.** Apparatus used for adsorption measurements. SO_2 is stored in the round
768 glass flask, the powdered ash sample is in the sample tube. When the valve between
769 sample and SO_2 reservoir is opened, the pressure drops due to adsorption of SO_2 on
770 the sample surface. The amount of adsorbed SO_2 can be calculated from the
771 magnitude of the pressure drop.

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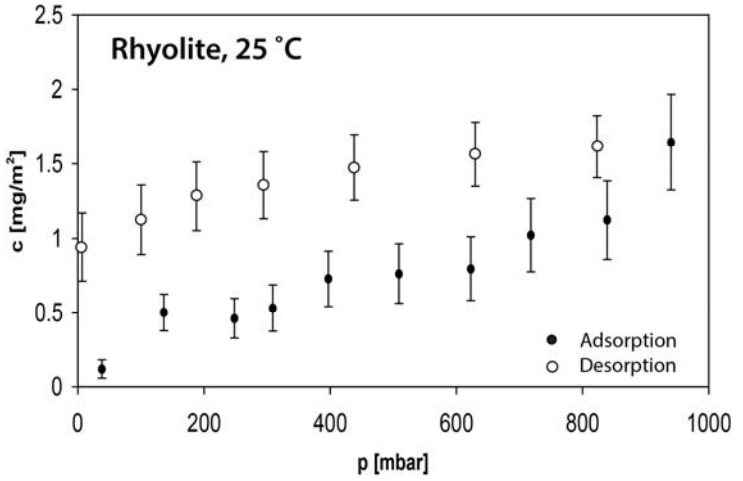

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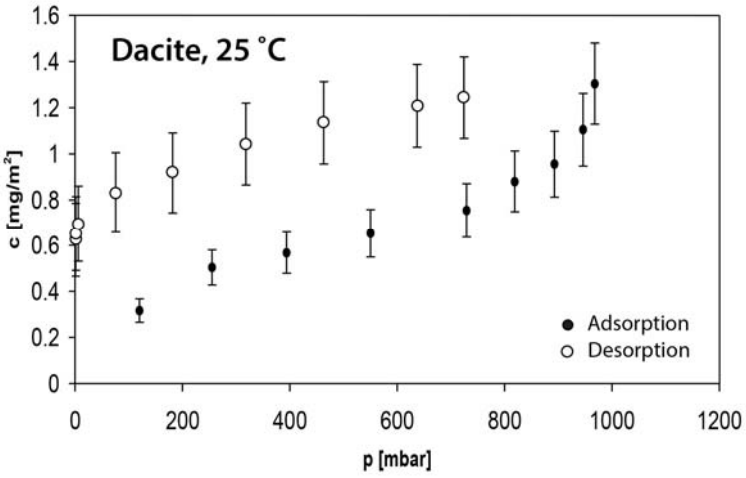

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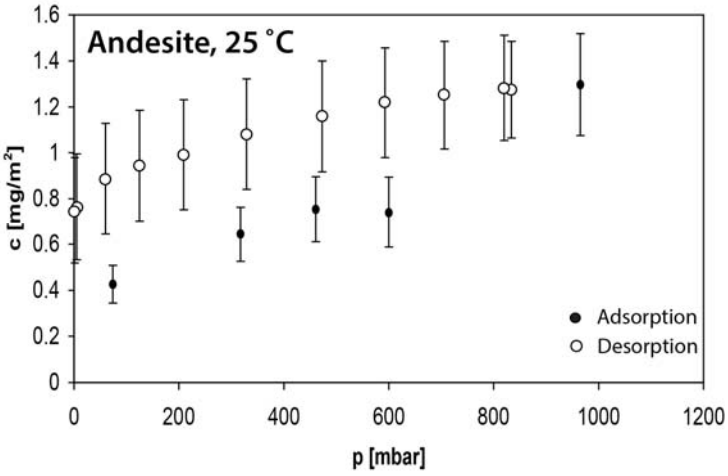

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775 **FIGURE 2.** Adsorption and desorption isotherms of SO_2 on glass powders of
776 rhyolitic, dacitic and andesitic composition at 25 ˚C. Surface concentrations are given
777 in mg per m^2 surface area. The shape of the adsorption curves corresponds to a "type
778 II" isotherm in the classification of Brunauer (1945); see text for further discussion.
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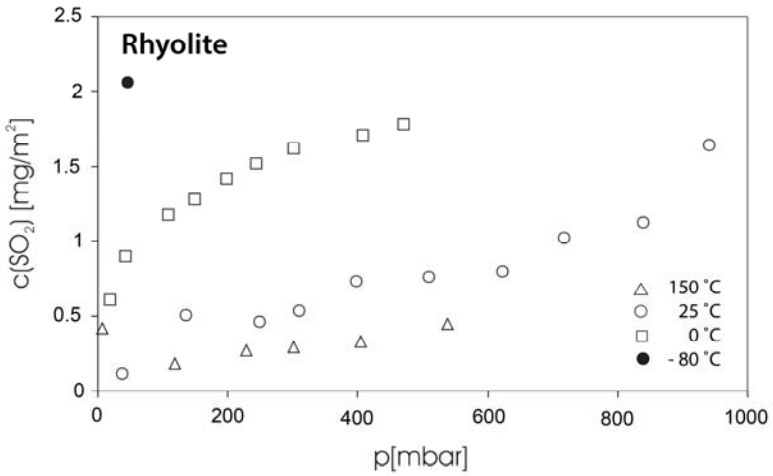
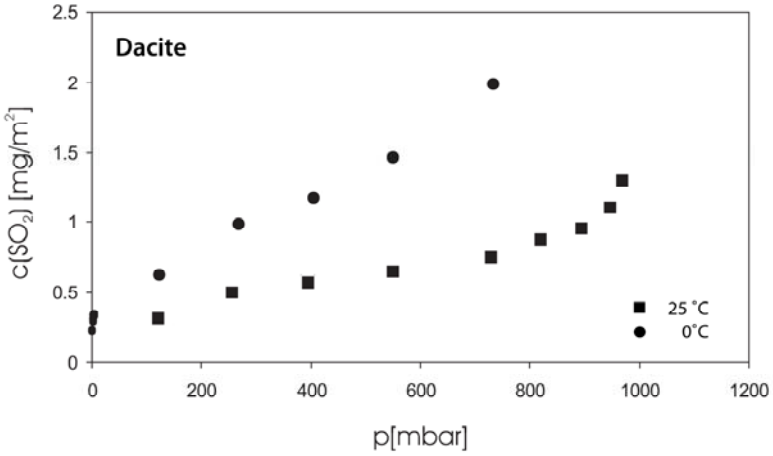




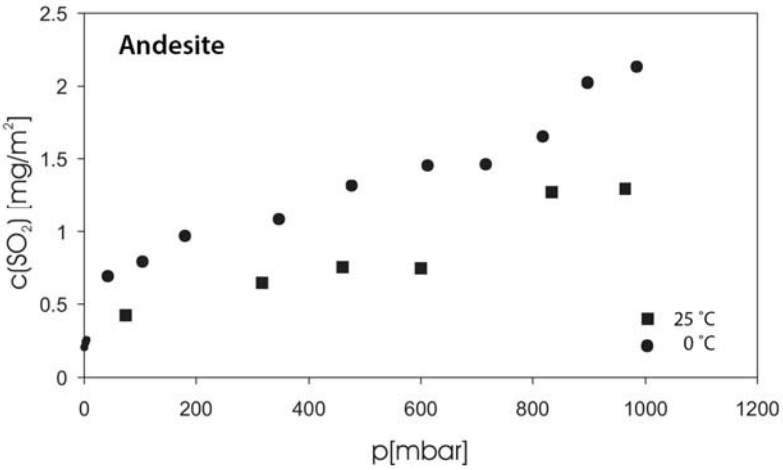
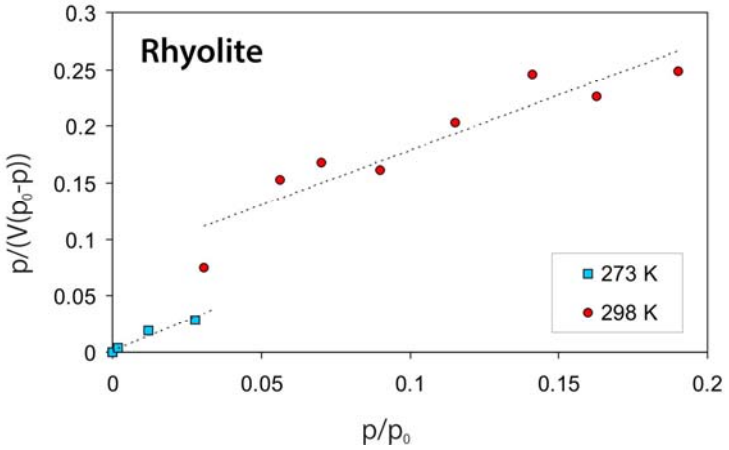
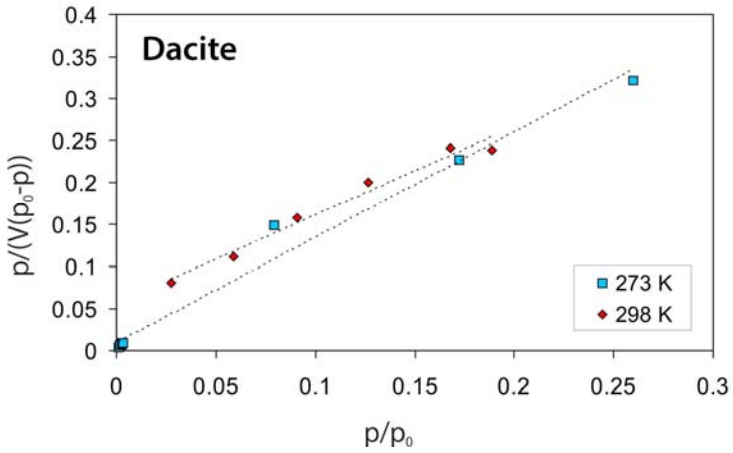


FIGURE 3. Adsorption isotherms of SO_2 on rhyolite, dacite and andesite glass powder at different temperatures. Adsorption decreases with temperature. Relative errors in measured surface concentration are approximately 20 %.





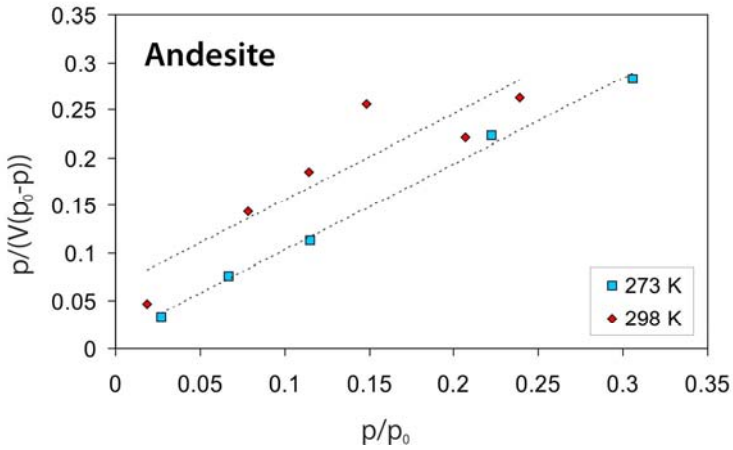
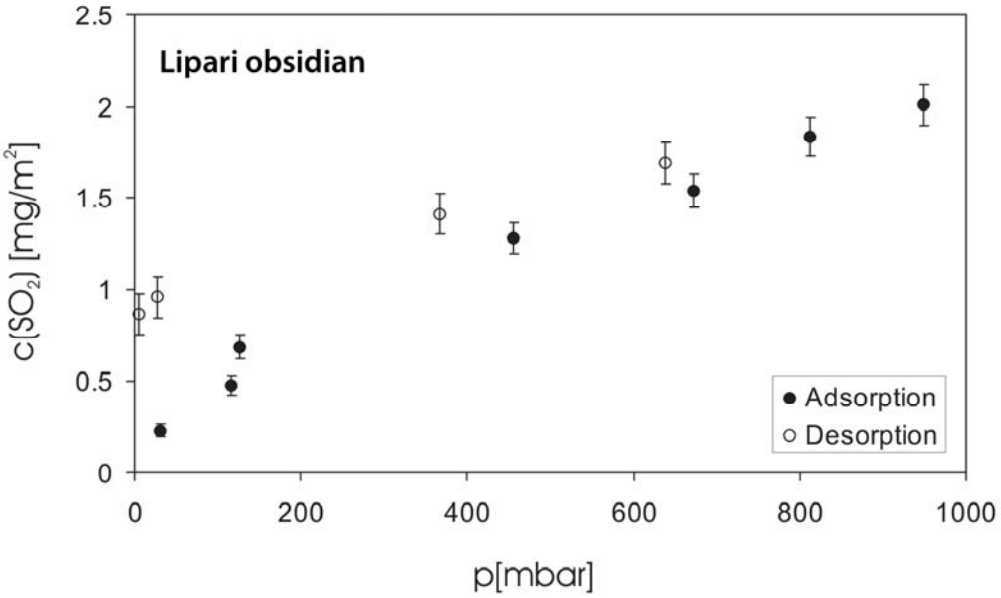


FIGURE 4. BET plots of the adsorption isotherms of SO_2 on rhyolitic, dacitic and andesitic glasses at 0 ˚C and at 25 ˚C. V is the volume of adsorbed SO_2 (under standard pressure and temperature) in cm^3/g, p is pressure in mbar and p_0 is the condensation pressure. In this diagram, an adsorption isotherm following the BET equation should plot on a straight line.



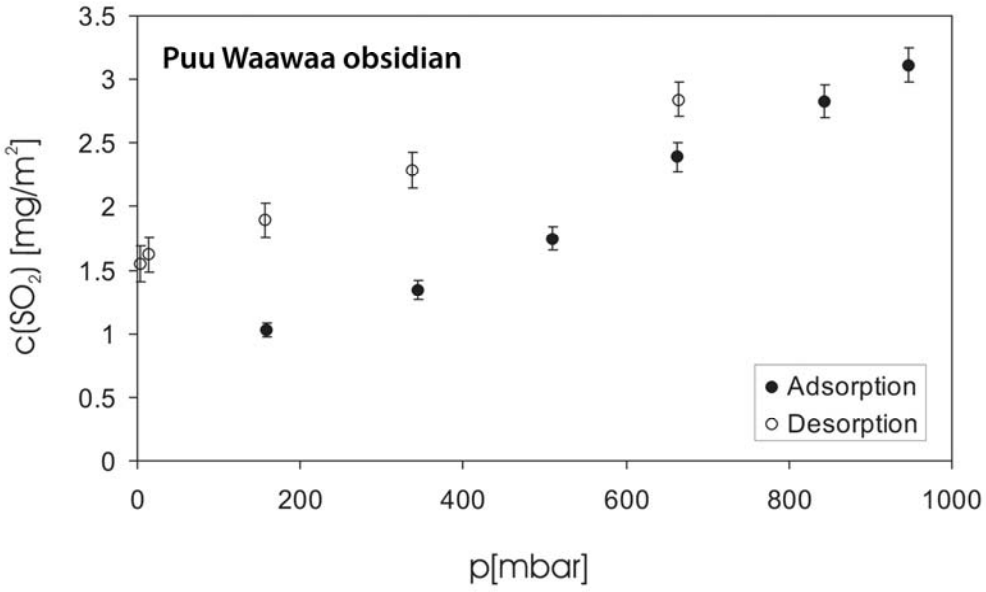


FIGURE 5. Adsorption and desorption isotherms of SO_2 on powder samples of two natural obsidians, measured at 0˚C. The Lipari obsidian (Eolian islands, Italy) is rhyolitic in composition, the Puu Waawaa (Hawaii) obsidian is trachytic.

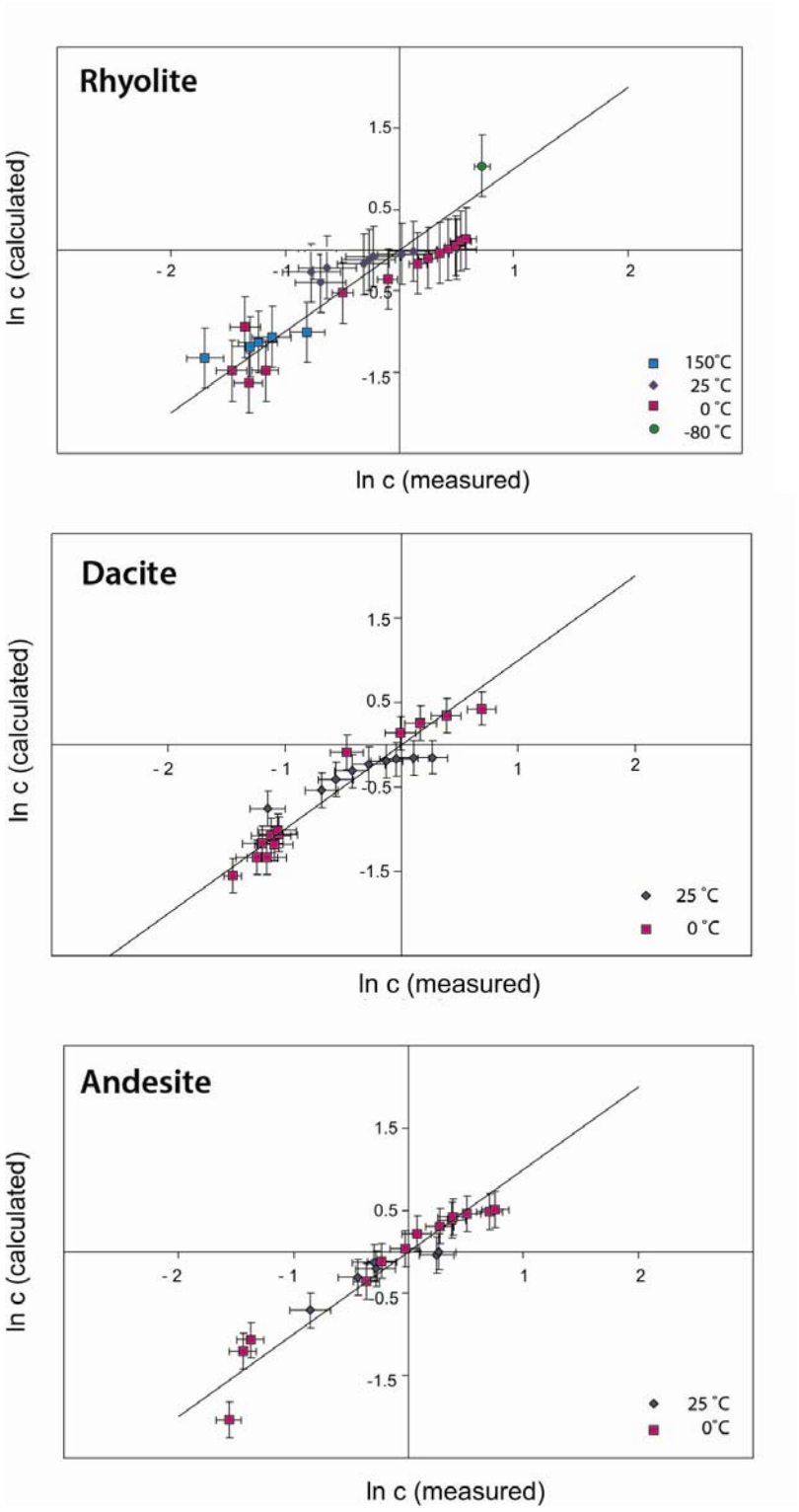
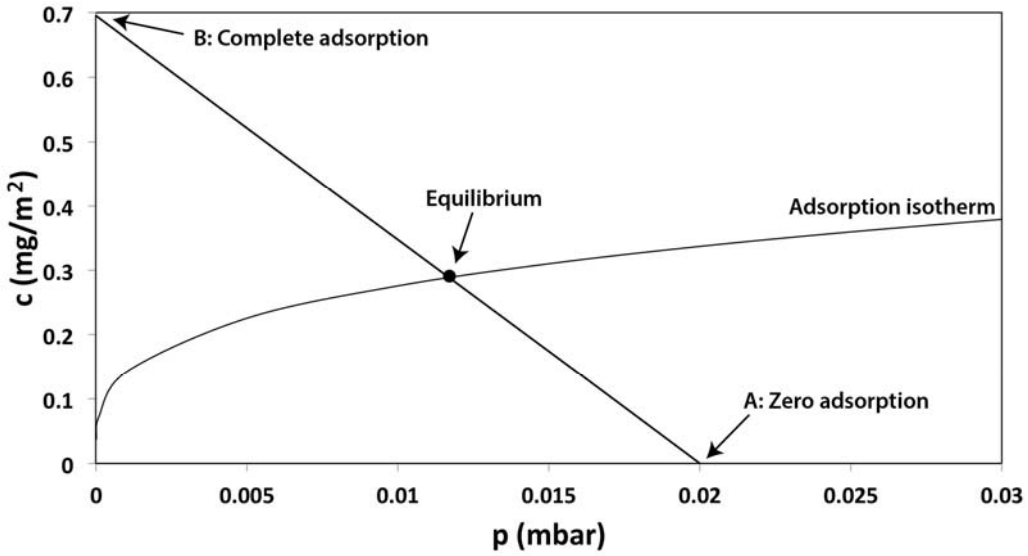


FIGURE 6. Comparison of predicted and measured surface concentrations of SO_2 on rhyolitic, dacitic and andesitic glasses. Surface concentrations in mg/m^2. Error bars for the measurements are the same as in Fig. 2, the errors in the calculated values are derived from the uncertainties in the regression parameters, as given in Table 4.



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810 **FIGURE 7.** Calculated isotherm for the adsorption of SO_2 on andesite glass at 220 K
811 (-53 ˚C). The amount of adsorbed SO_2 in equilibrium can be found by the intersection
812 of the isotherm with a straight line connecting the points corresponding to zero
813 adsorption (A) and to complete adsorption (B), respectively. This straight line
814 represents a mass balance for the adsorption process. Assumptions: Specific ash
815 surface of 2500 m^2/kg, weight ratio of volcanic gas (mostly water vapor) to ash of
816 0.05, 1 mole %, SO_2 in the volcanic gas, ratio of air to volcanic gas in the plume 100:
817 1, altitude 10 km. This translates into an initial partial pressure of SO_2 in the diluted
818 plume of 0.02 mbar. For details, see text.

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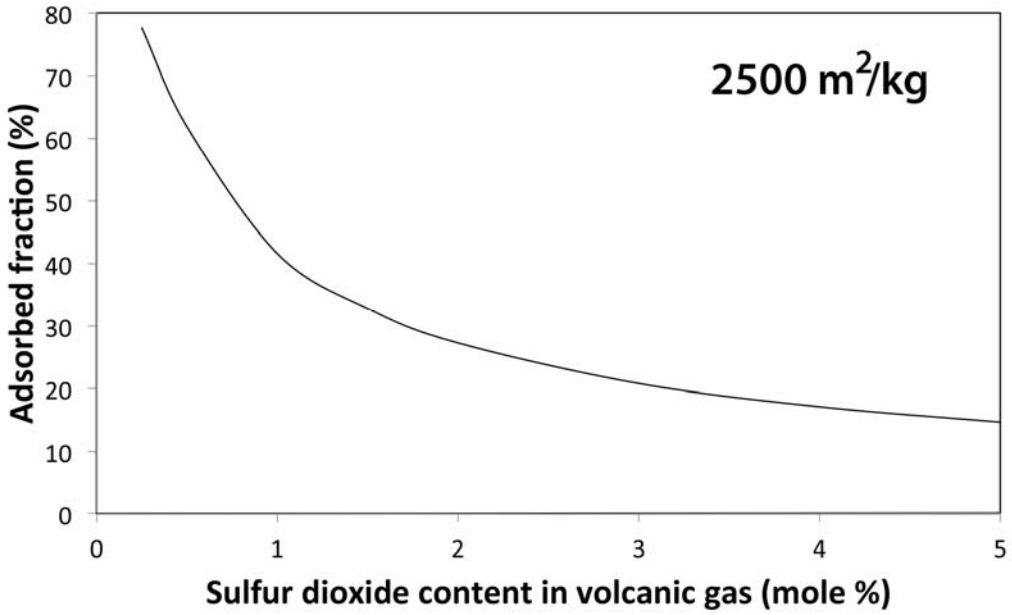

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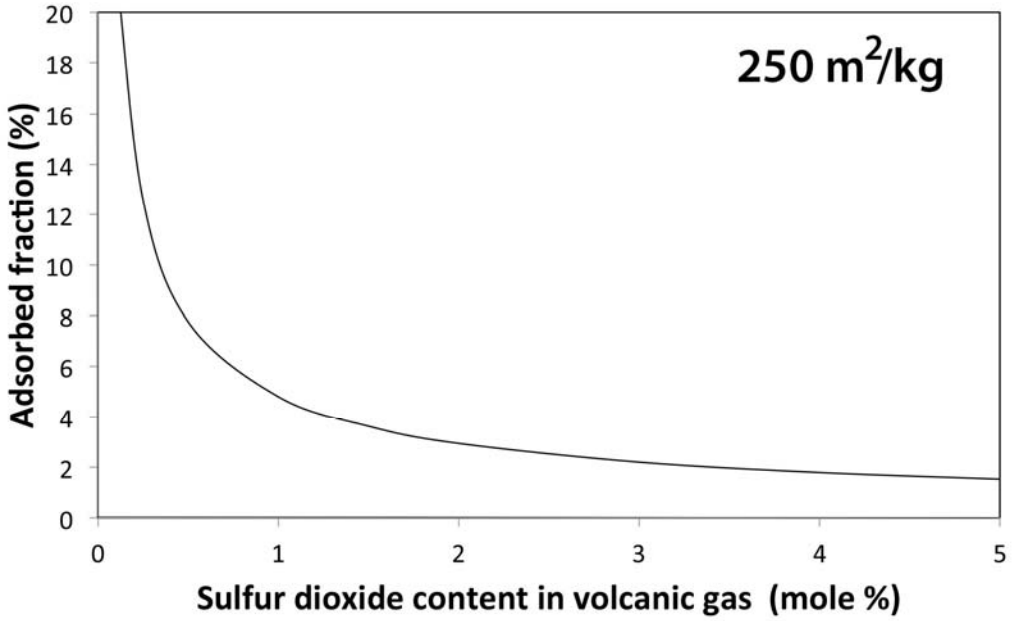

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825

826 **FIGURE 8.** Fraction of SO_2 adsorbed on the surface of ash in a volcanic plume as a
827 function of initial SO_2 content, for two different specific surfaces of the ash (2500
828 m^2/kg and 250 m^2/kg). Assumptions: Weight ratio of volcanic gas to ash of 0.05, ratio
829 of air to volcanic gas in the plume 100: 1, altitude 10 km, temperature 220 K, ash of
830 andesitic composition.

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