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1	The adsorption of HCl on volcanic ash
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4	
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7	
8	Abstract. Understanding the interaction between volcanic gases and ash is important
9	to derive gas compositions from ash leachates and to constrain the environmental
10	impact of eruptions. Volcanic HCl could potentially damage the ozone layer, but it is
11	unclear what fraction of HCl actually reaches the stratosphere. The adsorption of HCl
12	on volcanic ash was therefore studied from -76 to + 150 $^{\circ}$ C to simulate the behavior
13	of HCl in the dilute parts of a volcanic plume. Finely ground synthetic glasses of
14	andesitic, dacitic, and rhyolitic composition as well as a natural obsidian from
15	Vulcano (Italy) served as proxies for fresh natural ash. HCl adsorption is an
16	irreversible process and appears to increase with the total alkali content of the glass.
17	Adsorption kinetics follow a first order law with rate constants of $2.13 \cdot 10^{-6} \text{ s}^{-1}$ to
18	$1.80 \cdot 10^{-4} \text{ s}^{-1}$ in the temperature range investigated. For dacitic composition, the
19	temperature and pressure dependence of adsorption can be described by the equation
20	$\ln c = 1.26 + 0.27 \ln p - 715.3/T$ , where c is the surface concentration of adsorbed HCl
21	in mg/m <sup>2</sup> , T is temperature in Kelvin, and p is the partial pressure of HCl in mbar. A
22	comparison of this model with a large data set for the composition of volcanic ash
23	suggests that adsorption of HCl from the gas phase at relatively low temperatures can
24	quantitatively account for the majority of the observed Cl concentrations. The model
25	implies that adsorption of HCl on ash increases with temperature, probably because of

26	the increasing number of accessible adsorption sites. This temperature dependence is
27	opposite to that observed for SO <sub>2</sub> , so that HCl and SO <sub>2</sub> are fractionated by the
28	adsorption process and the fractionation factor changes by four orders of magnitude
29	over a temperature range of 250 K. The assumption of equal adsorption of different
30	species is therefore not appropriate for deriving volcanic gas compositions from
31	analyses of adsorbates on ash. However, with the experimental data provided here, the
32	gas compositions in equilibrium with the ash surfaces can be calculated. In particular,
33	for dacitic composition, the molar ratio of S/Cl adsorbed to the ash surface is related
34	to the molar S/Cl ratio in the gas phase according to the equation $\ln (S/Cl)_{adsorbed} =$
35	2855 $T^{-1}$ + 0.28 ln (S/Cl) <sub>gas</sub> – 11.14. Our data also show that adsorption on ash will
36	significantly reduce the fraction of HCl reaching the stratosphere, only if the initial
37	HCl content in the volcanic gas is low (< 1 mole %). For higher initial HCl
38	concentrations, adsorption on ash has only a minor effect. While HCl scavenging by
39	hydrometeors may remove a considerable fraction of HCl from the eruption column,
40	recent models suggest that this process is much less efficient than previously thought.
41	Our experimental data therefore support the idea that the HCl loading from major
42	explosive eruptions may indeed cause severe depletions of stratospheric ozone.
43	
44	Keywords: Adsorption, ash, hydrogen chloride, volcanic gases, ozone
45	
46	1. Introduction
47	The short-term climatic impact of volcanic eruptions is mostly due to the interaction
48	of sulfur and halogen species in volcanic gases with the atmosphere. The surface
49	cooling observed after major explosive eruptions is caused by the injection of sulfur
50	dioxide into the stratosphere, where it is photochemically oxidized to sulfate aerosols.

51 These aerosols backscatter sunlight and may remain in the stratosphere for months or 52 even years (e.g. McCormick et al. 1995, Robock 2000). Ozone destruction is another 53 potential effect of large explosive eruptions, but it is much less understood than the 54 surface cooling effect. Black et al. (2014) suggested that the end-Permian mass 55 extinction partially resulted from ozone depletion associated with the Sibirian Trap 56 magmatism. Measurable depletions in stratospheric ozone were observed after the 57 1991 Mt. Pinatubo eruption (Brasseur and Granier 1992, Solomon et al. 1998). They 58 were attributed to the catalytic effect of sulfate aerosol surfaces, which may enhance 59 the concentration of active chlorine species involved in ozone destruction (Solomon et 60 al. 1993, Hofmann et al. 1994). However, another mechanism could be the direct 61 injection of volcanic hydrogen chloride (HCl) into the stratosphere. A study by 62 Tabazadeh and Turco (1993) suggested that this mechanism is inefficient, because 63 hydrogen chloride would be nearly completely washed out of the eruption column by 64 condensing water. More recent models of eruption plumes (Textor et al. 2003), 65 however, show that most of the water in the plume is present as solid ice, which 66 greatly reduces the efficiency of HCl scavenging. Moreover, most of the ice particles 67 are lifted upwards, so that more than 25 % of the HCl originally contained in the 68 plume may reach the stratosphere. This prediction was confirmed for the case of a 69 high-latitude eruption by direct sampling of a volcanic cloud from Hekla volcano 70 (Rose et al. 2006, Millard et al. 2006). Spectroscopic observations also suggested an 71 increase of 40 % in the total column of HCl above 12 km altitude after the 1982 El 72 Chicón eruption (Mankin and Coffey 1984, see also Woods et al. 1985), while at most 73 a slight increase in stratospheric HCl was observed after the 1991 Mt. Pinatubo 74 eruption (Mankin et al. 1992, Wallace and Livingston 1992). Kutterolf et al. (2013) 75 estimated the Cl and Br release from 14 large explosive eruptions in Nicaragua in the

76last 70 00 years and concluded that most of these eruptions likely caused significant77ozone destruction in the stratosphere. On the other hand, elevated HCl concentrations78are only rarely detected in ice cores; this may, however, be due to the volatilization of79HCl in the presence of  $H_2SO_4$  (Wagnon et al., 1999, Zdanowicz et al. 1999, Thamban80et al. 2006). The limited data available may imply that the stratospheric HCl yield of81eruptions varies considerably, depending on initial gas composition and on the82processes occurring in the eruption column.

83

84 Hydrogen chloride (HCl) concentrations in volcanic gases typically range from < 0.0585 to > 5 mole %, with most data probably in the 0.1 to 1 mole % range (Symonds et al. 86 1994, Fischer 2008). Relatively high HCl concentrations and HCl/SO<sub>2</sub> ratios are often 87 found in arc volcanoes. Estimated annual fluxes of HCl vary widely, from 0.4 to 170 88 Tg/a (Symonds et al. 1988, Halmer et al. 2002). Pyle and Mather (2009) used a 89 compilation of measured HCl/SO<sub>2</sub> ratios and total SO<sub>2</sub> fluxes to estimate the HCl flux 90 from arc volcanoes at  $4.3 \pm 1$  Tg/a, which is believed to dominate the global flux. 91 However, the flux of HCl reaching the stratosphere is certainly much lower, because 92 only large eruptions penetrate the tropopause and processes in the eruption column 93 may deplete HCl. While the depletion by water and ice has already been investigated 94 in some detail, little is known about the possible effect of HCl adsorption on volcanic 95 ash (Rose 1977). Ayris et al. (2014) studied the interaction of HCl with ash under 96 near-vent, high-temperature conditions (200 - 800 °C). Only for alkali-rich tephrite 97 and phonolite glasses, reaction with HCl to NaCl was observed, but not for dacite and 98 rhyolite. The very short residence time of ash at near-vent conditions during an 99 explosive eruption may further limit the extent of adsorption at high temperature. This 100 suggests that HCl adsorption, if it is an important process at all, must occur in the

101 low-temperature portion of the dilute plume. We therefore studied the adsorption of
102 HCl on ashes of rhyolitic, dacitic, and andesitic composition from -76 to + 150 °C at
103 variable HCl partial pressures covering the plausible conditions in a dilute volcanic
104 plume.

105

### 106 **2. Experimental methods**

107 Fe-free synthetic glasses of rhyolitic, dacitic, and andesitic composition were used as

108 proxies for fresh volcanic ash. The glasses were prepared from homogenized,

stoichiometric mixtures of analytical grade SiO<sub>2</sub>, Al(OH)<sub>3</sub>, MgO, CaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>,

and  $K_2CO_3$ . After decarbonation in a platinum crucible, the charge was melted at

111 1600 °C for 1 hour and quenched in deionized water, yielding a clear glass with some

bubbles. Microprobe analyses are given in Table 1. The glass was then dried and

113 ground four times for seven minutes each in a planetary mill. No liquid was added to

114 avoid adsorption on fresh surfaces. The surface area of the powders was determined

115 with a Quantachrome instrument by measuring the BET adsorption isotherm of

116 krypton at 77 K. To constrain the isotherm, seven data points were measured in a

117 range of pressures ranging from 5 to 30 % of the condensation pressure of Kr. 100 –

118 200 mg of sample were outgassed at 200 °C for 24 hours before the measurement.

119 The specific surfaces obtained were in the range of  $1.5 - 4.9 \text{ m}^2/\text{g}$ . These numbers are

120 quite comparable to those obtained for fine (< 100  $\mu$ m) natural ash (mostly 1.1 – 2.1

121  $m^2/g$  for a sieved fraction < 100  $\mu$ m; Demelle et al. 2005; 4.3  $m^2/g$  for

122 phreatomagmatic ash from Eyafjallajökull; Gislason et al. 2011).

123

124 Adsorption measurements were carried out in a glass apparatus equipped with a

125 Vacuubrand DVR 5 pressure gauge, following the procedure described by Schmauss

126 and Keppler (2014). In brief, 30 - 50 g of the sample powder were placed in a sample 127 tube and the entire system was evacuated. HCl gas was then filled into a reservoir 128 flask up to the desired pressure. Once the valve between the sample tube and the 129 reservoir was opened, an instantaneous pressure drop occurred due to the expansion 130 of the gas into the sample tube, followed by a slow decrease in pressure due to the 131 adsorption of HCl on the sample surface. From the known volumes of the system, the 132 measured pressure drop and the temperature, the amount of adsorbed HCl can be 133 calculated. All required formulae are given by Schmauss and Keppler (2014). For 134 calculating the amount of adsorbed HCl, the ideal gas law was used, which is a very 135 good approximation for HCl under the low pressures and the temperatures of interest. 136 Once the pressure in the system had stabilized, the valve between sample and gas 137 reservoir was closed and the pressure in the reservoir was increased. After opening 138 the valve again, the next point of the adsorption isotherm was measured. This 139 procedure was repeated until the pressure in the system reached nearly one bar. 140 Desorption experiments started from close to one bar by decreasing the pressure in the 141 reservoir with a vacuum pump. After opening the valve to the sample, pressure first 142 increased, due to expansion of the gas from the sample tube to the reservoir, followed 143 by a slow increase due to desorption of HCl from the sample surface. After pressure 144 stabilized, the valve between reservoir and sample was closed and the procedure was 145 repeated, until the pressure in the reservoir was close to zero mbar. Measuring an 146 entire adsorption and desorption cycle for a sample took several weeks. Experiments 147 at 150 °C were carried out by immersing the sample tube in an oil bath; for 148 experiments at -76 °C, the sample tube was cooled with a mixture of dry ice and 149 acetone. Main sources of error in the surface concentrations are the specific surfaces 150 of the powders, the pressures, and the volumes in the system.

152 Wet chemical analyses were carried out in order to confirm the measured HCl surface 153 concentrations. About 10 g of HCl-loaded glass sample were mixed with 100 ml of 154 distilled water and stirred for 24 hours in a closed Erlenmeyer flask. The solution was 155 then filtered off and some NaHCO<sub>3</sub> added to adjust to neutral pH. Chloride was then 156 determined by titrating against a 0.1 N AgNO<sub>3</sub> solution with Ag<sub>2</sub>CrO<sub>4</sub> as endpoint indicator (Mohr method). Surface concentrations (in  $mg/m^2$ ) were then obtained by 157 158 dividing the mass of measured HCl by the surface area of the sample according to the 159 BET data. 160 161 3. Results 162 163 3.1. Kinetics of adsorption Figure 1 shows the experimentally observed decrease of pressure during an adsorption 164 165 experiment. For every adsorption step, the data can be described by an equation 166  $(p - p_{eq}) = (p_0 - p_{eq}) e^{-\lambda_t}$ 167 (1) 168 where p is pressure,  $p_{eq}$  is the equilibrium pressure, and  $p_0$  is the initial pressure after 169 170 opening the valve between gas reservoir and sample;  $\lambda$  is the rate constant and t is time. Values of  $p_{eq}$  and of  $\lambda$  were obtained by fitting equation (1) to the data for every 171 172 adsorption step. Since in the ideal gas law, pressure is proportional to the number of 173 moles in the gas phase,  $(p - p_{eq})$  is proportional to the number of gas atoms n that still

174 will be absorbed and  $(p_0 - p_{eq})$  is proportional to the initial number of gas atoms  $n_0$ 

that ultimately will end up on the sample surface. The above equation (1) is thereforeequivalent to a first-order-law of reaction kinetics

177

$$n = n_0 e^{-\lambda t}$$
 (2)

179

180 with the same rate constant  $\lambda$  as in equation (1).

181

182 Experimentally determined rate constants are compiled in Table 2; measured values for  $\lambda$  range from 2.13  $\cdot$  10<sup>-6</sup> s<sup>-1</sup> to 1.80  $\cdot$  10<sup>-4</sup> s<sup>-1</sup>. The timescale for reaching 183 184 equilibrium is in the order of magnitude of the inverse of these rate constants. For 185 dacite at room temperature, a clear decrease of  $\lambda$  with the initial gas pressure of the 186 adsorption experiment is observed. This may be related to the fact that in the 187 experiments at higher pressure, the most reactive surface sites had already been 188 saturated with HCl in the previous steps of the adsorption experiment. In other words, 189 with increasing surface coverage of the sample, the rate of adsorption decreases. This 190 effect is not so clearly seen for the other samples. Interestingly, the rate constants for 191 HCl adsorption on dacite at -76 °C are in most cases higher than at room temperature. 192 This is unexpected, as reaction rates should generally increase with temperature. 193 However, as will be discussed below, only the most reactive surface sites seem to be 194 accessible for HCl adsorption at -76 °C, and this higher reactivity probably also 195 translates into higher rate constants. Desorption experiments also followed a first-196 order-kinetics, with rate constants similar to those for adsorption on the same sample. 197 However, only very little desorption was generally observed and therefore, desorption 198 kinetics will not be further discussed.

#### 200 *3.2. Adsorption isotherms*

201 Adsorption and desorption isotherms of HCl for andesitic, dacitic and rhyolitic 202 glasses are shown in Figure 2. With increasing pressure, the amount of HCl adsorbed 203 on the surface first increases sharply and then levels off and reaches a plateau. This 204 behavior corresponds to a type I adsorption isotherm in the Brunauer classification 205 (Brunauer et al. 1940), which is typical for a chemisorption process, where the 206 adsorbed molecule forms strong chemical bonds with the substrate. Above about 500 207 mbar, there is a slight further increase in surface concentration that may indicate 208 minor multilayer adsorption.

209

210 The desorption isotherms show that the adsorption process is nearly irreversible, i. e. 211 the surface concentration of HCl remains nearly constant when pressure is decreased 212 to zero mbar. This behavior is again consistent with a chemisorption process 213 involving the formation of strong chemical bonds between HCl and the substrate. The 214 HCl surface concentration observed for andesitic and rhyolitic glasses are rather 215 similar, while those for the dacite glass are 2 to 3 times higher. Inspection of Table 1 216 shows that this effect cannot be due to the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO or MgO contents of the 217 glass, since the percentage of these components in the dacite glass is between that for 218 rhyolite and andesite. However, the total alkali  $(Na_2O + K_2O)$  content of the dacite is 219 significantly higher than for the other two compositions. Since the alkalis are the 220 strongest bases in the system, it is plausible that they enhance the reaction with the 221 acidic HCl molecule. This is consistent with the enhanced reactivity of alkali-rich 222 glasses with HCl vapor at high-temperature, near vent conditions (Ayris et al. 2014). 223 Note, however, that the alkali contents of the synthetic glasses used for this study are

not necessarily representative of a global average of rhyolite or dacite compositions
and individual rhyolites may very well have higher total alkalis than some dacites.

227	The temperature dependence of HCl adsorption was explored for dacite, by carrying
228	out additional experiments at -76 °C and at 150 °C. The results are shown in Figure 3.
229	Adsorption increases with temperature, probably because at low temperature
230	adsorption occurs only on some particularly reactive sites, with the number of
231	available sites increasing with temperature. This is a typical behavior sometimes
232	observed for chemisorption, where the formation of chemical bonds requires some
233	activation energy that can only be overcome above a certain temperature (e.g. Batzill
234	2006, Duran-Munoz et al. 2013).
235	
236	The surface concentrations of HCl remaining on the samples after the end of the
237	desorption experiments, as derived from the measurements of the isotherms, were
238	checked by argentometric titration of leachate solutions, with generally good
239	agreement (Supplementary Table S1). Only the dacite sample from the experiment at
240	room temperature may have lost some HCl by handling on humid air before the
241	argentometric analysis. For the comparison, the surface concentrations were
242	converted into wt. % using the specific surfaces given in Table 1.
243	

244 *3.3. A regression model for the adsorption of HCl on dacite glass* 

Schmauss and Keppler (2014) showed that the temperature and pressure dependence
of the adsorption of SO<sub>2</sub> on volcanic ash may be described by a modified Freundlich

247 isotherm

249 
$$\ln c = A T^{-1} + B \ln p + C$$
 (3)

251	where c is the surface concentration in $mg/m^2$ , T is temperature in K and p is the
252	partial pressure of the absorbed gas in mbar. A least squares fit of all the experimental
253	data for HCl adsorption on dacite glass using the same equation yielded A = -715.3 $\pm$
254	55.3, B = $0.27 \pm 0.03$ , and C = $1.26 \pm 0.29$ , with R <sup>2</sup> = 0.93. A comparison of
255	measured and predicted surface concentrations of HCl is shown in Figure 4.
256	
257	3.4. HCl adsorption on a natural obsidian sample
258	In order to test whether the adsorption data obtained by using synthetic samples are
259	also applicable to natural, Fe-bearing volcanic glasses, we also measured the
260	adsorption of HCl on a natural alkali-rhyolitic obsidian from the 1739 AD eruption of
261	Vulcano (Aeolian Islands, Italy; see Table1). This obsidian contains a small fraction
262	of feldspar microlites. In adsorption experiments at room temperature, both the
263	kinetics of adsorption and the adsorption isotherm were found to be quite similar to
264	the synthetic glasses (Fig. 5). The HCl surface concentrations observed for the
265	Vulcano obsidian are somewhat higher than for the synthetic rhyolite and resemble
266	more those for synthetic dacite (Fig. 2). This is, however, entirely consistent with the
267	elevated bulk alkali content in this sample, supporting the idea that this is the primary
268	compositional parameter influencing HCl adsorption.
269	
270	
271	4. Discussion
272	

274 The experiments in the present study were carried out in the presence of HCl alone, 275 while in the volcanic plume, H<sub>2</sub>O is usually the most abundant component, together 276 with smaller amounts of SO<sub>2</sub>, HCl and traces of other gases. CO<sub>2</sub> may be an abundant species as well, but since the CO<sub>2</sub> molecule lacks a permanent dipole moment, its 277 278 absorption on surfaces can likely be ignored. The much more important question is 279 therefore, whether the data obtained in the present study may be applied to the 280 situation in a volcanic plume, where HCl is a minor component compared to  $H_2O$ . 281 Very likely this is possible, because the glass powders used in the experiments described here were exposed to air of average humidity at ambient conditions during 282 283 the preparation of the experiments. Both studies on synthetic silicate glasses and of 284 volcanic ashes show that under ambient conditions and also in a volcanic plume, the 285 surface of a glass particle will be covered with a complete layer of adsorbed H<sub>2</sub>O 286 molecules (Razouk and Salem 1948, Delmelle et al. 2005). Accordingly, there should 287 be no difference in HCl surface concentration between the glass powders studied here 288 in pure HCl alone and the adsorption of HCl on ash in the volcanic plume. 289 Dissolution of HCl gas in liquid water adhering to ash particles is a separate effect, 290 which will be discussed below.

291

Figure 6 compares Cl concentrations adsorbed on the surface of volcanic ashes from more than 40 individual eruptions with the experimental data for dacite glass obtained in this study. To convert surface concentrations (in mg/m<sup>2</sup>) into bulk concentrations (mg Cl / kg ash), the specific surface area of the ash has to be assumed. Figure 6 shows predicted maximum bulk concentrations (vertical lines) for two different specific surfaces of 1 m<sup>2</sup>/g, which is at the low end of this parameter for fine ash (Demelle et al. 2005; Gislason et al. 2011) and 0.1 m<sup>2</sup>/g, more characteristic for 299 coarser ash (see supplementary Table S2 for examples). The vertical lines in Figure 6 300 give maximum concentrations achievable at a given specific surface and temperature 301 at high HCl partial pressures. However, inspection of Figure 3 shows that similar 302 concentrations may already be reached at low HCl partial pressures (10 - 100 mbar) 303 realistic for a volcanic plume. Figure 6 shows that adsorption of HCl from the gas 304 phase can account for the vast majority of the observed Cl concentrations. Only the 305 data for Irazu and San Miguel appear anomalously high, but they could still be 306 explained by surface adsorption if the specific surface of these ashes were higher, in the order of  $2 - 4 \text{ m}^2/\text{g}$ , within the range confirmed by measurements on fine ashes 307 308 (Demelle et al. 2005; Gislason et al. 2011). More likely, however, theses ashes 309 contain Cl from some other source, e.g. from hydrothermal alteration. Alteration 310 processes may also have contributed some Cl to other samples. The data shown in 311 Figure 6 are completely consistent with earlier experimental results for fluorine. 312 Oskarsson (1980) already concluded that the fluorine concentrations adsorbed on ash 313 may be explained by adsorption from the gas phase at relatively low temperatures near 200 °C. 314

315

316 In a volcanic plume, ash may interact with aerosols or become coated by films of 317 liquid water or ice. Rose (1977) suggested that the accumulation of aerosol particles, particularly of H<sub>2</sub>SO<sub>4</sub> is a main source for adsorbed material on ash. However, H<sub>2</sub>SO<sub>4</sub> 318 319 aerosols are usually only a minor species, subordinate to SO<sub>2</sub> in volcanic plumes close 320 to the vent (e.g. Mather et al. 2006). Delmelle et al. (2007; see also Gislason et al. 321 2011) detected Cl and S on the surface of ash particles by X-ray photoelectron 322 spectroscopy, but not by SEM. They concluded that Cl and S form coatings with a 323 thickness of a few nm at most; they further suggested that this observation together

324 with the observed surface depletion in Na, K, Mg, and Ca argues against the 325 deposition of material via aerosols, but is more consistent with precipitation from a 326 liquid film. However, their data are equally consistent with our model of direct 327 adsorption from a gas phase, since the shape of the adsorption isotherms indeed 328 suggests the formation of a mono-molecular layer of HCl on the ash surface. Coating 329 of ash particles by water certainly occurs in some parts of the plume, but this process 330 is reversible. Once the water evaporates, the dissolved HCl and SO<sub>2</sub> will also be lost, 331 unless some surface reaction has occurred. However, if the surface is in equilibrium 332 with the liquid film and the liquid is in equilibrium with a gas phase, then the surface 333 is also in direct equilibrium with the gas. In other words, this process should lead to 334 the same surface concentration as observed in our experiments. The fact that surface 335 reactions, but not the solubility in liquid water determine the origin of leachable 336 material on ash surfaces is also supported by the observation of a systematic offset 337 between S/Cl ratios adsorbed on ash and S/Cl ratios in rainwater (Edmonds et al., 338 2003). If the relative solubility of SO<sub>2</sub> and HCl in liquid water somehow determined 339 the S/Cl ratio on the ash surface, this ratio should be the same as in rainwater that had 340 interacted with the plume.

341

342

#### 343 *4.2 Deriving volcanic gas compositions from adsorbate analyses*

344 The analysis of volatile species adsorbed on fresh ash surfaces is a convenient and

345 frequently used method to infer volcanic gas compositions (e.g. Rose 1977, Williams

et al. 1986, Armienta et al. 1998, de Hoog et al. 2001, Armienta et al. 2010, Bagnato

et al. 2011, 2013). Usually, the implicit assumption is made that the concentration

ratio of adsorbed S, Cl, and F is somehow comparable to the molar ratio of the

349	corresponding species in the gas phase of the plume. Our experimental data, together								
350	with published results for the adsorption of SO <sub>2</sub> on volcanic ash (Schmauss and								
351	Keppler, 2014) allow testing this assumption. The adsorption of HCl and SO <sub>2</sub> can								
352	likely be treated independently, without considering direct interactions, because the								
353	concentration of these gases, particularly in the dilute part of the plume, is very low								
354	and therefore, none of them will fully cover the glass surface. Moreover, the								
355	experimental data of this study and of Schmauss and Keppler (2014) suggest that HCl								
356	and SO <sub>2</sub> actually react with different surface sites, since both the dependence of								
357	adsorption on glass composition and on temperature are very different. For SO <sub>2</sub> , glass								
358	composition has little influence on adsorption, while the total alkali content seems to								
359	control the reactivity with HCl. HCl adsorption increases with temperature, while the								
360	adsorption of SO <sub>2</sub> decreases with temperature.								
361									
362	Schmauss and Keppler (2014) showed that SO <sub>2</sub> adsorption on dacite glass can be								
363	described by the equation								
364									
365	$\ln c_{SO2} = 2140 \text{ T}^{-1} + 0.29 \ln p_{SO2} - 9.32 \tag{4}$								
366									
367	while in the present study, we observed that HCl adsorption follows the equation								
368									
369	$\ln c_{\rm HCl} = -715.3 \ {\rm T}^{-1} + 0.27 \ \ln p_{\rm HCl} + 1.26 \tag{5}$								
370									
371	In both equations, the coefficient in front of the ln p term is indistinguishable within								
372	experimental error. If one assumes an average coefficient of 0.28, both equations can								
373	be combined to								

375 
$$\ln (c_{SO2}/c_{HC1})_{adsorbed} = 2855 \text{ T}^{-1} + 0.28 \ln (p_{SO2}/p_{HC1}) - 10.58$$
(6)

376

At the low pressures involved, the ratio of the partial pressures  $p_{SO2}/p_{HC1}$  is virtually identical with the SO<sub>2</sub>/HCl molar ratio in the gas. To convert the ratio of surface concentrations  $c_{SO2}/c_{HCl}$ , which are given in mg/m<sup>2</sup>, into a molar ratio of S/Cl, the numbers have to be divided by the ratio of the molar masses of SO<sub>2</sub> and HCl. This adds a linear term of - ln (64.06/36.46) = - 0.56 to the equation, which then becomes: ln (S/Cl)<sub>adsorbed</sub> = 2855 T<sup>-1</sup> + 0.28 ln (S/Cl)<sub>gas</sub> - 11.14 (7)

385 where S/Cl now refers to the molar ratio in the gas and on the glass surface.

386

387 Figure 7 shows the ratio of S/Cl on dacitic ash surfaces, as predicted by equation 7 for 388 a range of temperatures and gas compositions. Obviously, the adsorbed S/Cl ratio is a 389 very strong function of temperature. In fact, the temperature effect is much stronger 390 than the effect of the S/Cl ratio in the gas. For example, near 0 °C, increasing the S/Cl 391 ratio in the gas by a factor of 10 has the same effect on the absorption as reducing 392 temperature by less than 20 °C. The relatively small effect of gas composition is due 393 to the factor of 0.28 in front of the  $\ln (S/Cl)_{gas}$  term in equation (7); it implies that 394 under otherwise equal conditions, (S/Cl) in the adsorbate only increases by a factor of  $(S/Cl)_{gas}^{0.28}$ , i.e. a 10-fold increase in this ratio in the gas phase only translates into a 395 396 less than 2-fold increase in the adsorbate. The 0.28 exponent is related to the effect 397 seen in Figure 2 that the amount of adsorbed HCl first increases sharply at low p<sub>HCl</sub>, 398 but then levels off at higher p<sub>HCl</sub>. The strong effect of temperature on the adsorbed

399 S/Cl ratio is obviously related to the opposite temperature dependence for HCl and 400 SO<sub>2</sub> adsorption. The decrease of adsorption with temperature for SO<sub>2</sub> (Schmauss and 401 Keppler 2014) is the normal behavior expected for adsorption. This is because in the 402 expression for the Gibbs free energy  $\Delta G = \Delta H - T\Delta S$  for the adsorption reaction, the 403  $-T\Delta S$  term increases with temperature and should therefore shift the equilibrium to 404 the side with higher entropy; the entropy of a molecular species is always higher in 405 the gas phase than adsorbed on a surface. The increase in HCl adsorption with 406 temperature is therefore very unusual, but this kind of behavior is sometimes observed 407 for chemisorption (e.g. Batzill 2006, Duran-Munoz et al. 2013), i.e. if the adsorption 408 process involves the formation of strong chemical bonds. In such a situation, an activation energy may have to be overcome for the reaction, so that only a fraction of 409 410 sites is involved in the adsorption process at low temperature, while this fraction 411 increases at higher temperatures. Once all possible surface sites are activated, 412 adsorption should decrease upon further increase with temperature, because of the 413 thermodynamic argument mentioned above. Accordingly, the data presented here for 414 HCl adsorption and equation 7 should not be extrapolated to temperatures far above 415 those for which they were calibrated (i.e. beyond 150 °C).

416

The strong temperature effect on adsorption as shown in Figure 7 needs to be taken into account whenever volcanic gas compositions are to be derived from analyses of volatile species adsorbed on ash surfaces. This means that estimates of volcanic fluxes of HCl that were obtained from  $SO_2$  flux measurements scaled by the S/Cl ratio in adsorbates should be treated with considerable caution; the same may also apply to other gas species. The frequently made assumption of equal adsorption of different species is only valid under very specific conditions (see also Bagnato et al. 2011). For 425 resulting in an S/Cl ratio of 1 also in the adsorbate, only occurs at a temperature near

426 -20 °C. However, for an S/Cl ratio in the gas of 10, the temperature where no

- 427 fractionation occurs decreases to near -50 °C.
- 428

429 The conclusions reached here on the strong effect of temperature on the fractionation 430 of SO<sub>2</sub> and HCl during adsorption are actually quite consistent with a number of field 431 observations. S/Cl ratios of ashes vary widely, < 0.01 to > 100, and often by orders of magnitude even within the same eruption (see Supplementary Table 2). This is likely 432 433 not only due to variations in gas composition, but also to the fractionation of S and Cl 434 between gas and ash. Edmonds et al. (2003) measured the SO<sub>2</sub>/HCl ratio of gases 435 from three eruption periods of the Soufrière Hills volcano on Montserrat between 436 1996 and 2002, using both open path infrared spectroscopy and the analysis of ash 437 leachates. For the phase I and phase II major dome building periods, a SO<sub>2</sub>/HCl molar 438 ratio near 0.1 was spectroscopically detected in the plume and ash analyses gave 439 similar (although more scattered) numbers. This is consistent with Figure 7, which 440 suggests that for an S/Cl ratio of 0.1, no fractionation occurs between ash and gas 441 phase near + 30  $^{\circ}$ C – a very plausible temperature for a low-altitude tropospheric 442 plume in a tropical climate. Bagnato et al. (2013) studied ash leachates of the 2010 443 Eyafjallajökull eruption on Iceland and found major discrepancies between the S/Cl 444 ratio adsorbed on ash surfaces and that measured in the volcanic gases. For the highly 445 explosive phase III eruption, S/Cl ratios from ash leachates are mostly between 0.4 446 and 0.6, while direct gas measurements yielded significantly higher molar S/Cl ratios 447 of 1.5 - 3.3. Inspection of Figure 7 suggests that these data may be reconciled by 448 assuming a temperature of adsorption near 0 °C, quite plausible for a tropospheric

449 plume during spring in Iceland. Note that these ash samples were taken at horizontal 450 distances from the vent up to more than 50 km, where the plume will have cooled 451 down to ambient atmospheric temperature; closer to the vent, larger variations in 452 adsorbed S/Cl ratio are observed, which may be related to variations in plume 453 temperature and also plume height (4 - 9 km; Petersen et al. 2012). Even larger 454 fractionations of S and Cl between ash and gas were observed for the basaltic fire 455 fountain phase; the S/Cl ratio in the gas was measured to be between 5 and 25 while a 456 molar ratio of S/Cl of 0.14 was measured on the ash. According to Figure 7, this could imply equilibration between gas and ash at temperatures around + 50 °C, which is 457 458 plausible for a fire fountain eruption, as there may be very significant radiative 459 heating of particles after they left the vent and the plume likely entrained less ambient air than for the highly explosive phase III. 460 461

462 In the previous discussion, we have referred to Figure 7, which is based on equation 7 463 and strictly valid only for a dacitic composition. Glass composition will have some 464 effect on the S/Cl fractionation, which needs to be considered. However, this effect is 465 much smaller than the variation due to temperature. For a given gas composition, 466 Figure 7 suggests variations in the ratio of adsorbed S and Cl by four orders of 467 magnitude over just 250 °C. Compared to this, the compositional effect on the amount 468 of adsorbed HCl (Fig. 2) is only about a factor of 2 and the effect of glass 469 composition on SO<sub>2</sub> adsorption is even smaller (Schmauss and Kepper 2014). 470 Therefore, we believe that the conclusions derived from comparing the curves in 471 Figure 7 with ash leachate analyses are at least approximately correct, although 472 additional calibrations of the effect of ash composition on the S/Cl fractionation 473 between plume gas and ash surface are certainly desirable. In general, our discussion

474 shows that a large part of the apparent discrepancies between gas composition and the 475 composition of gas leachates can be accounted for by the effect of temperature on 476 adsorption. This does not rule out that other factors, in particular alteration processes 477 may also be important under some circumstances. However, for fresh, unaltered ash it 478 may indeed be possible to derive gas compositions from leachate analyses, if 479 reasonable estimates of plume temperature can be made. Moreover, on a local scale 480 close to a vent, the S/Cl ratio may actually provide a sensitive thermometer for the 481 temperature in the plume.

482

483 *4.3. Stratospheric HCl yield and ozone depletion* 

484 With the experimental data on HCl adsorption obtained in this study, the fraction of volcanic HCl reaching the stratosphere during Plinian eruptions can be better 485 486 constrained. As noted above, HCl adsorption increases with temperature, at least up to 487 150 °C. Accordingly, one may suspect that most of the adsorption may occur in the 488 relatively hot parts of the volcanic plume. However, ascent velocities in a typical Plinian eruption column are  $> 100 \text{ m s}^{-1}$  (Textor et al. 2006), implying that ash 489 490 particles reach the stratosphere within 1 - 2 minutes. This very much limits the time available for high-temperature, near-vent interaction between volcanic gases and ash. 491 492 The highest rate constant for HCl adsorption measured in this study (Table 4) was 1.8  $10^{-4}$  s<sup>-1</sup>. For a residence time of 120 s, this would allow only 2 % of the equilibrium 493 494 surface concentration to be adsorbed on the ash. Accordingly, it is likely that most of 495 the adsorption occurs in the dilute parts of the volcanic plumes after it has cooled 496 down to the ambient temperature at the respective altitude.

498 A rough estimate of the magnitude of HCl adsorption can be obtained by considering 499 the HCl surface concentration that would result from the (hypothetical) total 500 adsorption of all the HCl in the plume. This concentration is simply the ratio of the 501 total mass of HCl in the plume to the total available surface area of the ash. According 502 to Woods and Bursik (1991) fine ash with a grain size  $< 100 \mu$ m accounts for  $> 50 \mu$ m. 503 % of total deposit for Plinian eruptions. Measurements of fine ash samples from various volcanoes yielded specific surfaces of  $1.1 - 2.1 \text{ m}^2/\text{g}$  (Delmelle et al. 2005). 504 505 The ash is produced by the exsolution of gas bubbles, which ultimately disrupt and 506 fragment the melt. Subduction zone magmas that are responsible for the most 507 prominent explosive eruptions typically have pre-eruptive water contents near 5 wt. % 508 (e.g. Métrich and Wallace 2008). Water is also the main component of the gas plume, 509 with HCl concentrations ranging from < 0.05 to > 5 mole %, the majority of data probably being in the 0.1 to 1 mole % range (Symonds et al. 1994, Fischer 2008). 510 511 These data from volcanic gases are in rough agreement with the Cl/H<sub>2</sub>O ratio in melt 512 inclusions from primitive arc basalts (Métrich and Wallace 2008). If one therefore 513 assumed a mass ratio of volcanic gas to (glassy) ash of 0.05 (equivalent to 5 % H<sub>2</sub>O in the pre-eruptive magma), 1 mole % HCl in the gas and a surface of  $1 \text{ m}^2/\text{g}$  for the 514 total ash (or 50 % of fine ash with 2  $m^2/g$ ), adsorbing all the HCl on the ash would 515 vield a surface concentration of  $1.01 \text{ mg/m}^2$ . Comparing this number to the 516 experimental data in Figure 2 and 3 suggests that such surface concentrations may be 517 518 easily reached at room temperature or above; however, they may not be achievable at 519 the much lower temperatures prevailing in the stratosphere. The situation would be very different, however, for an initial HCl concentration in the gas of 0.1 mole %; the 520 corresponding surface concentration of  $0.10 \text{ mg/m}^2$  is easily reached even at low 521 522 temperatures and at low HCl partial pressure. This rough calculation already shows

that the initial HCl concentration in the plume, which likely reflects the pre-eruptive
Cl/H<sub>2</sub>O ratio in the magma, largely controls the fraction of HCl sequestered by ash
and therefore, together with scavenging by hydrometeors, the effective stratospheric
HCl loading.

527

528 For a fully quantitative treatment of HCl adsorption, the equilibrium between the gas 529 phase and ash surface as described by equation (5) has to be considered together with 530 mass balance constraints under the conditions prevailing in the umbrella part of a 531 volcanic plume. For our calculations, we assume a plume model similar to that 532 described by Textor et al. (2006). The umbrella part of the plume is located at an 533 altitude near 20 km with a temperature around 220 K, containing about 100 g of ash 534 per kg of plume mixture. Assuming an initial gas mass fraction in the erupting 535 material of 5 wt. % (see above), this implies a dilution of volcanic gases by entrained 536 air by a factor of 200. The calculations are, however, rather insensitive to this dilution factor, since according to equation (5), adsorption only increases with  $p_{HCI}^{0.27}$ , i.e. a 537 ten-fold increase in the dilution factor would only decrease adsorption by a factor of 538 539 1.9. For a volcanic gas with 1 mole % HCl, the partial pressure of HCl decreases from 540 10 mbar at the vent to 0.0022 mbar in the umbrella cloud by the combined effects of 541 the increasing altitude and dilution by entrained air. This number does not include 542 possible scavenging of HCl by hydrometeors (see Textor et al. 2003). Under the given 543 conditions, equation (5) predicts a concentration of HCl adsorbed on the surface of ash of 0.026 mg/m<sup>2</sup> in equilibrium with this HCl partial pressure, less than 3 % of the 544  $1.01 \text{ mg/m}^2$  required for total adsorption (see above). Since during the adsorption 545 546 process, the partial pressure of HCl in the gas decreases until equilibrium is reached, 547 the real number for the equilibrium surface concentration is slightly smaller.

Following the method described by Schmauss and Keppler (2014), one obtains 548 virtually the same value of  $0.026 \text{ mg/m}^2$ . This number appears small, but the resulting 549 bulk Cl concentration (26-52 mg/kg for a specific surface of 1-2  $m^2/g$ ) overlaps well 550 551 with the low end of concentrations reported for natural ashes (Fig. 6). Stratospheric 552 ash samples are likely under-represented in Figure 6, because many eruptions did not 553 reach the stratosphere and even for large eruptions, the ashes likely contain particles 554 that did not reach the stratosphere. For less explosive eruptions, particle velocities are 555 smaller and the plume may be less diluted by entrained air. Ash might therefore be 556 exposed to higher HCl partial pressures for longer times and at higher temperatures, 557 leading to stronger adsorption. This is a possible explanation for the fact that the 558 surface concentrations predicted for adsorption in the stratosphere are at the lower end 559 of the data for natural ash samples. However, the physical conditions for adsorption 560 likely vary considerably between individual eruptions and are influenced by 561 parameters such as the actual wind field that are hard to include in general models. 562

563 The calculation above clearly shows that for high initial HCl concentrations (> 1 564 mole %) in the gas phase of a Plinian eruption, adsorption by ash does not 565 significantly reduce the stratospheric HCl loading. However, the adsorption effect 566 becomes significant for low initial HCl concentrations. For example, for an initial HCl content in the volcanic gas of 0.1 mole %, an equilibrium surface concentration 567 of  $0.013 \text{ mg/m}^2$  is obtained, 13 % of the value required for total absorption (see 568 569 above). The relationship between HCl content in the initial volcanic gas and the 570 adsorption on ash is illustrated in Figure 8. Physically, this relationship is due to the 571 fact that the total amount of HCl in the plume increases proportionally to the initial 572 HCl molar fraction and therefore the HCl partial pressure; however, the amount of

573 HCl adsorbed on ash only increases with  $p_{HCl}^{0.27}$  so that at higher  $p_{HCl}$ , the fraction of 574 HCl that is not removed by adsorption increases. In general, the efficiency of 575 adsorption on ash surfaces in dilute eruption plumes is much smaller for HCl than for 576 SO<sub>2</sub> (Schmauss and Keppler 2014).

577

578 The pre-eruptive Cl contents and Cl/H<sub>2</sub>O ratios in subduction zone volcanics tend to 579 be high (Métrich and Wallace 2008, Kutterolf et al. 2013). Accordingly, HCl contents 580 in the fluid phase near 1 mole % and higher will be common for Plinian eruptions in 581 subduction zone settings. In such a situation, HCl adsorption on ash will not be able to 582 significantly reduce the amount of HCl reaching the stratosphere. Although there is 583 still much work to be done to understand these processes, previous studies (Textor et 584 al. 2003) have suggested limited efficiency of HCl scavenging by liquid water and by 585 ice in the eruption column, with more than 25 % of the total HCl reaching the 586 stratosphere. Our results therefore support the hypothesis that significant and perhaps 587 even catastrophic ozone depletion due to the HCl yield of giant eruptions is possible 588 (Kutterolf et al. 2013, Black et al. 2014).

589

#### 590 **5.** Conclusions

591 The interaction of volcanic gases with ash particles could potentially limit the

environmental impact of explosive eruptions. We provide new experimental data on

593 the kinetics and thermodynamics of HCl adsorption on volcanic ash. Unlike for SO<sub>2</sub>,

- 594 HCl adsorption increases with temperature, so that large temperature-dependent
- 595 fractionations between HCl and SO<sub>2</sub> occur during the adsorption process. Extracting
- 596 volcanic gas compositions from analyses of ash leachates therefore requires

597 correcting for this effect. Although HCl adsorption increases with temperature, the

slow rate of the process implies that most of the adsorption occurs in the cold, dilute parts of a volcanic plume. For low initial HCl concentrations in the volcanic gas (0.1 mole % and below), the depletion of HCl by adsorption can be significant. However, for HCl concentrations of 1 mole % and above, adsorption on ashes is unlikely to reduce the stratospheric HCl yield of Plinian eruptions. Therefore, it appears quite plausible that the HCl yield of large explosive eruptions may cause significant ozone depletion in the stratosphere.

605

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611

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- 748

- 749 **Table 1**
- 750 Chemical composition (wt. %) and specific surface A  $(m^2/g)$  of synthetic glass
- samples and of a natural obsidian from Vulcano (Aeolian Islands, Italy) used for
  - Rhyolite Dacite Dacite Dacite Andesite Vulcano Batch 1 Batch 2 Batch 3 Obsidian SiO<sub>2</sub> 76.45 (83) 67.08 (30) 67.02 (49) 66.68 (71) 56.77 (18) 73.47 (35)  $Al_2O_3$ 12.37 (53) 16.49 (21) 16.81 (23) 16.96 (32) 21.63 (13) 13.49 (22)  $Fe_2O_3(t)$ 1.86 (13) MgO 3.14 (24) 4.96 (15) 4.97 (23) 5.14 (37) 7.31 (16) 0.11 (04) CaO 0.80 (07) 2.80 (10) 2.93 (11) 2.86 (16) 7.46 (10) 0.83 (10) Na<sub>2</sub>O 2.77 (08) 4.31 (09) 4.20 (05) 4.46 (09) 3.88 (09) 4.42 (08) K<sub>2</sub>O 3.33 (05) 3.15 (06) 3.00 (06) 2.92 (07) 1.77 (06) 5.10 (05) Total 98.86 98.79 98.93 99.02 98.82 99.28 А 3.82 4.90 1.50 2.74 3.01 2.97
- adsorption experiments

Numbers in parentheses are one standard deviation in the last digits.  $Fe_2O_3$  (t) is the

total iron content given as  $Fe_2O_3$ . For dacite, three batches of sample were prepared.

Batch 1 was used for experiments at room temperature, batch 2 at 150 °C, and batch 3

at -76 °C. Note that the synthetic compositions do not necessarily correspond to

757 global averages of the respective rock type.

# 758 **Table 2**

 Andesite		Dacite						Rhyolite	
T = 22 °C		T = - 76 °C		T = 22 °C		T = 150 °C		T = 22 °C	
 p (mbar)	$\lambda (10^{-6} \text{ s}^{-1})$	p (mbar)	$\lambda (10^{-6} \text{ s}^{-1})$	p (mbar)	$\lambda (10^{-6} \text{ s}^{-1})$	p (mbar)	$\lambda (10^{-6} \text{ s}^{-1})$	p (mbar)	$\lambda (10^{-6} \text{ s}^{-1})$
 68	124 (48)	58	58.5 (3.6)	42	180 (24)	104	44.4 (1.3)	80	45.4 (5.5)
105	52.1 (11.2)	86	103 (9)	147	32.1 (1.4)	95	15.9 (0.5)	125	57.0 (9.7)
185	44.3 (9.3)	123	96.7 (6.4)	197	12.0 (0.3)	315	14.8 (1.1)	191	149 (3)
374	28.2 (8.1)	206	99.4 (6.3)	306	5.98 (1.41)	424	6.92 (0.28)	243	37.7 (13.7)
581	42.8 (11.4)	299	103 (7)	528	6.32 (0.27)	538	25.4 (0.3)	371	43.0 (17.0)
721	117 (23)	529	92.6 (10.7)	692	7.58 (0.72)	798	21.8 (25.8)	506	46.3 (14.1)
852	58.6 (10.2)	723	66.2 (30.0)	794	2.75 (7.06)	956	18.1 (19.0)	713	34.0 (12.6)
982	36.4 (15.7)	935	76.1 (23.3)	965	2.13 (0.43)			967	37.3 (14.5)

759 Rate constants  $\lambda$  for the adsorption of HCl on glass surfaces

760 p is the initial pressure of HCl vapor to which the sample was exposed in each step. The pressures are listed in the sequence of the steps of the

adsorption experiment. Numbers in brackets are estimated uncertainties.





**Fig. 1.** Kinetics of HCl adsorption on dacitic glass at room temperature and for an

initial pressure  $p_0 = 179$  mbar. Pressure in the system decreases exponentially, until

equilibrium is reached.



Fig. 2. HCl adsorption and desorption isotherms for (a) and esitic, (b) dacitic, and (c)





Fig. 3. Effect of temperature on the adsorption of HCl on dacite glass. Error bars areone standard deviation.



In  $C_{_{HCI}}$  (measured)





**Fig. 5.** HCl adsorption on a natural obsidian from the 1739 A.D. eruption of Vulcano (Aeolian Islands, Italy). a) Kinetics of adsorption at room temperature for an initial pressure of  $p_0 = 138$  mbar. The decrease in pressure can be described by a rate constant of  $\lambda = 1.28 \cdot 10^{-5} \text{ s}^{-1}$ ; b) Adsorption and desorption isotherms at room temperature. Error bars are one standard deviation. The point at the highest pressure may have been affected by some unknown experimental problem.



790 Fig. 6. Concentrations of chlorine adsorbed on volcanic ashes from recent eruptions 791 (see supplementary Table S2 for data and sources). The data are compared with the 792 maximum surface concentrations according to the experimental data for HCl 793 adsorption on dacite glass (vertical lines), assuming two different specific surface areas (1  $m^2/g$  for fine ash, 0.1  $m^2/g$  for coarser ash) and adsorption at three different 794 795 temperatures (150 °C, 21 °C, -76 °C). Note that some samples may contain a 796 contribution of Cl-bearing alteration products from other sources, e.g., evaporites, 797 marine aerosols or pre-eruptive interaction with saline groundwaters, altered dome 798 rocks or recycled volcanic ejecta.









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**Fig. 8.** Fraction of HCl adsorbed on volcanic ash in the umbrella part of a

805 stratospheric plume as a function of initial HCl concentration in the volcanic gas.

Assumptions: Plume altitude 20 km, temperature 220 K, dilution factor 200.