

# 1 Ozone depletion in tropospheric volcanic plumes

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5 [1] We measured ozone (O<sub>3</sub>) concentrations in the atmo-  
6 spheric plumes of the volcanoes St. Augustine (1976),  
7 Mt. Etna (2004, 2009) and Eyjafjallajökull (2010) and found  
8 O<sub>3</sub> to be strongly depleted compared to the background at  
9 each volcano. At Mt. Etna O<sub>3</sub> was depleted within tens of  
10 seconds from the crater, the age of the St. Augustine plumes  
11 was on the order of hours, whereas the O<sub>3</sub> destruction in the  
12 plume of Eyjafjallajökull was maintained in 1–9 day old  
13 plumes. The most likely cause for this O<sub>3</sub> destruction are  
14 catalytic bromine reactions as suggested by a model that  
15 manages to reproduce the very early destruction of O<sub>3</sub> but  
16 also shows that O<sub>3</sub> destruction is ongoing for several days.  
17 Given the observed rapid and sustained destruction of O<sub>3</sub>,  
18 heterogeneous loss of O<sub>3</sub> on ash is unlikely to be important.  
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## 23 1. Introduction

24 [2] Volcanoes have long been recognised as major sour-  
25 ces for gases and particles for the atmosphere. However for  
26 many years little attention was paid to their impact on the  
27 oxidation capacity of the troposphere. *Bobrowski et al.*  
28 [2003] showed the presence of very large amounts of bro-  
29 mine oxide (BrO) radicals in the plume of Soufrière Hills,  
30 Montserrat during quiescent degassing. Several other studies  
31 found BrO in the plumes of other passively degassing vol-  
32 canoes [e.g., *Oppenheimer et al.*, 2006; *Bobrowski et al.*,  
33 2007] and satellite observation also confirmed the pres-  
34 ence of BrO in the plume of Kasatochi volcano after its  
35 explosive eruption in 2008 [*Theys et al.*, 2009]. From other  
36 parts of the atmosphere we know that BrO mixing ratios of  
37 1–10% of the values in volcanic plumes lead to very strong  
38 catalytic destruction of ozone (O<sub>3</sub>) [see, e.g., *von Glasow*  
39 *and Crutzen*, 2007], hence one would expect O<sub>3</sub> depletion  
40 also to occur in volcanic plumes.

41 [3] Very little data is available about O<sub>3</sub> in volcanic  
42 plumes mainly due to logistical difficulties of access and  
43 cross-sensitivities of many O<sub>3</sub> instruments to SO<sub>2</sub>: Broad-  
44 band instruments measuring integrated UV absorption may

have a positive interference with SO<sub>2</sub>, whereas wet-chemical  
53 methods as often used in balloon soundings have a negative  
54 cross-sensitivity on a mole-per-mole basis [*Schenkel and*  
55 *Broder*, 1982]. *Hobbs et al.* [1982] used an interference-  
56 free chemiluminescence technique and reported a 90%  
57 depletion of O<sub>3</sub> in the plume of Mt. St. Helens compared to  
58 the background air, however they give very little details on  
59 this. *Zerefos et al.* [2006] found a strong O<sub>3</sub> depletion in  
60 Mt. Etna's plume over Greece, however they used a wet-  
61 chemical technique so the lack of O<sub>3</sub> in their data might  
62 simply imply the presence of a volcanic SO<sub>2</sub> layer. O<sub>3</sub>  
63 depletion in stratospheric volcanic plumes has also been  
64 observed [e.g., *Rose et al.*, 2006].  
65

[4] A number of modelling studies [*Bobrowski et al.*, 2007;  
66 *Roberts et al.*, 2009; *von Glasow*, 2010] has aimed at  
67 reproducing the observed halogen radicals in volcanic plumes  
68 and predict significant O<sub>3</sub> destruction in the plume. The  
69 model used by *von Glasow* [2010] was initialised mainly  
70 based on observations at Mt. Etna. The results showed very  
71 strong O<sub>3</sub> destruction in volcanic plumes for the whole  
72 duration of the model runs (3 days). More details about  
73 reactive chemistry in volcanic plumes can be found in the  
74 recent review by *von Glasow et al.* [2009]. In this paper we  
75 present data from a variety of instruments, volcanic settings  
76 and different campaigns that clearly show a strong O<sub>3</sub>  
77 depletion in volcanic plumes.  
78

## 2. Field Sites and Methods

### 2.1. St. Augustine (February 1976)

[5] Airborne in situ O<sub>3</sub> data were collected by the Uni-  
81 versity of Washington (UW) Cloud and Aerosol research  
82 group during the January–February 1976 eruption of the  
83 St. Augustine Volcano, located in the lower Cook Inlet,  
84 southwest of Anchorage, Alaska.  
85

[6] Flight tracks were generally arranged as a series of  
86 cross plume traverses at different altitudes, designed to map  
87 out the plume vertical extent, or repeated passes through  
88 'puffs' as they moved downwind. More information on the  
89 B-23 sampling and the 1976 St. Augustine eruption is  
90 provided by *Hobbs et al.* [1977] and *Stith et al.* [1978, and  
91 references therein].  
92

[7] Ozone measurements were made with a commercial  
93 chemiluminescence O<sub>3</sub> analyzer (Monitor Labs model  
94 8410A), which measures O<sub>3</sub> by sensing light output from  
95 the reaction of O<sub>3</sub> with ethylene. This technique has no  
96 known interferences with volcanic gasses but might over-  
97 read O<sub>3</sub> by a few % at high humidities, so that our reported  
98 O<sub>3</sub> losses are lower limits. It had a response time of less than  
99 5s for 0 to 200 ppbv. The analyzer was calibrated with an  
100 UV-lamp-based calibrator (see *Hegg et al.* [1976] for more  
101 details).  
102

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tl.1 **Table 1.** Airborne Measurements of the O<sub>3</sub> Depletion in the Plume  
tl.2 of St. Augustine, 1976<sup>a</sup>

tl.3	Date	O <sub>3</sub> Loss	State	Distance	Alt	Part. Flux
tl.4	09 Feb	20–50%	BE			400
tl.5	11 Feb	67–87%	BE			200
tl.6	12 Feb	0%	BE			2
tl.7	13 Feb	44–89%	BE, ash	~24km	2.1–2.4km	60–3 × 10 <sup>5</sup>
tl.8	14 Feb	78–100%	PE	28–56km	1.8–2.4km	30–90
tl.9	16 Feb	52%	PE			60
tl.10	18 Feb	23–67%	PE	~56km	2.1–2.5	20–30

tl.11 <sup>a</sup>“O<sub>3</sub> loss” is relative depletion of O<sub>3</sub> compared to background measure-  
tl.12 ments, “Distance” is from the crater and “Alt” is the altitude above sea level.  
tl.13 “State” is the eruption state: ME - major eruption, BE - between eruptions,  
tl.14 PE - mostly post eruptive, ash - high ash loading and “Part. Flux” is the esti-  
tl.15 mated flux (or range of fluxes, when more than one measurement was made)  
tl.16 of particulate matter (in kg s<sup>-1</sup>) measured on a given day after *Stith et al.*  
tl.17 [1978].

## 103 2.2. Etna (2004, 2009)

104 [8] Mt. Etna, one of the largest volcanic gas point sources  
105 on Earth, was selected as archetype of open-vent persis-  
106 tently active basaltic volcanoes. The results reported here  
107 were acquired over two field campaigns in July–August  
108 2004 and July 2009. Our measurements were performed  
109 during phases of passive (quiescent) degassing activity from  
110 the volcano’s summit vents: The 2004 campaign was per-  
111 formed a few months prior to an effusive eruption affecting  
112 the volcano’s eastern flank, from 09 Sept 2004 to 08 March  
113 2005. The 2009 campaign was carried out only a few weeks  
114 after the end of the most recent eruption (the May 2008–July  
115 2009 effusive event). Etna’s average gas output during our  
116 observations was generally at (or somewhat below) the  
117 ordinary degassing style of the volcano and the Central and  
118 North East craters were the most actively degassing open  
119 vents.

120 [9] In the 2004 campaign, we deployed 19 diffusion tubes  
121 with the objective of determining atmospheric O<sub>3</sub> con-  
122 centrations near the summit craters as well as on the up- and  
123 downwind flanks. Diffusion tubes are passive air sampling  
124 devices that rely on the molecular diffusion of the species of  
125 interest through an entrapped air volume (for more details  
126 see the auxiliary material and *Aiuppa et al.* [2007]).<sup>1</sup>

127 [10] In 2009 we made O<sub>3</sub> measurements at the North East  
128 Crater and on the flanks of the South East and Central  
129 Craters which were at that point in the plumes of the North  
130 East and the Central Crater. We used an UV absorption  
131 instrument (2B Technologies, Boulder, CO, USA, model  
132 202) with CrO<sub>3</sub> scrubbers for SO<sub>2</sub> (EnSci, Boulder, CO,  
133 USA) as this instrument shows a strong positive cross-  
134 sensitivity to SO<sub>2</sub> (at the very high SO<sub>2</sub> concentrations near  
135 the craters) which absorbs in the same wavelength range.  
136 The uncertainty of the 2B instrument is about ± 2 ppbv.  
137 Additionally measurements of the aerosol size distribution  
138 were made with an optical particle counter (TSI, AeroTrac  
139 8220) with a size range of  $d = 0.3\text{--}10.0\ \mu\text{m}$ . The sampling  
140 efficiency at  $d = 0.3\ \mu\text{m}$  is reported as 50% and 100% at  
141  $d = 0.45\ \mu\text{m}$ .

## 142 2.3. Eyjafjallajökull (April–May 2010)

143 [11] The data from Eyjafjallajökull were collected  
144 between 20 April and 18 May 2010, when the BAe 146–301

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2010GL044997.

operated by the Facility for Airborne Atmospheric Mea- 145  
measurements (FAAM) made nine flights involving 45 transects 146  
of the Eyjafjallajökull plume, aged between 1 and 9 days 147  
old, as it was advected over the United Kingdom and 148  
northern France. The plume was generated via eruptive 149  
activity at Eyjafjallajökull, which commenced on 20 March. 150  
Lava extrusion through fissures resulted in Hawaiian style 151  
fire fountains, and generation of phreatomagmatic ash and 152  
gas plumes which rose up to 8 km. This event is publicly 153  
memorable for having resulted in an unprecedented closure 154  
of much of European airspace. Spatially, the plume, inter- 155  
sected during the measurements at altitudes between ~4– 156  
8 km, was highly heterogeneous often consisting of multiple 157  
layers, suggestive of the recirculation within the persisting 158  
high pressure system, as observed by a number of satellite 159  
instruments. 160

[12] SO<sub>2</sub> and O<sub>3</sub> were measured using Thermo Environ- 161  
mental Instruments Inc. Models 43 and 49C, respectively. 162  
The former is based on pulsed fluorescence and the latter on 163  
optical absorption. Contamination of the O<sub>3</sub> signal by 164  
atmospheric SO<sub>2</sub> is a known issue with such measurements; 165  
however in this case this does not apply as the 49C operates 166  
with dual cells: the reference and the sample, with the O<sub>3</sub> 167  
being chemically scrubbed in the former. The difference 168  
between observed absorption in both cases is used to infer 169  
the O<sub>3</sub> concentration. Therefore any interfering absorption 170  
from SO<sub>2</sub> is cancelled out. The lowest detectable limit of 171  
O<sub>3</sub> is 1 ppbv and the overall 2σ uncertainty is estimated at 172  
±3 ppbv. The SO<sub>2</sub> sensor is specified as having a lower than 173  
detection limit response to ambient ozone levels, ruling out 174  
cross-sensitivity in the opposite direction. The overall 175  
uncertainty for the SO<sub>2</sub> instrument is 7–10%. The design of 176  
the sample inlet for the gas analysers is such that no sig- 177  
nificant aerosol reaches the instruments; this has been con- 178  
firmed by inspection of the PTFE membrane filter fitted in 179  
the sample line immediately upstream. These data were 180  
augmented with simultaneously collected nephelometric 181  
proxies for plume mineral aerosol loading (from a separate 182  
inlet), derived from a three wavelength TSI Inc. 3563 unit. 183  
The inlet used with this instrument becomes increasingly 184  
inefficient for particles with diameter greater than approxi- 185  
mately 5 μm. The largest source of error in data from both 186  
Thermo instruments is likely to result from rapid changes 187  
in gas concentration as the instruments’ integration times 188  
are 30 and 50 seconds for O<sub>3</sub> and SO<sub>2</sub>, respectively. 189

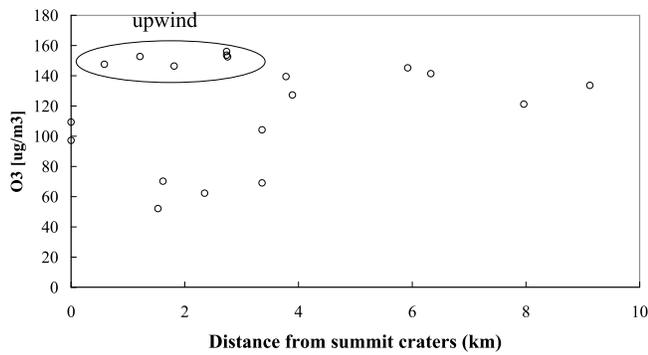
## 190 3. Results

### 191 3.1. St. Augustine

[13] A summary of the data from 27 plume interceptions 192  
is listed in Table 1 (all interceptions are shown in Table S1 193  
in the auxiliary material). The O<sub>3</sub> loss relative to the back- 194  
ground values is on average 60% but has a very large vari- 195  
ability (0–100%), which probably reflects differences in the 196  
plume composition on the different days but also different 197  
chemical processing due to different atmospheric condi- 198  
tions, e.g., mixing. 199

### 200 3.2. Etna

[14] The diffusion tube measurements at Mt. Etna in 2004 201  
(Figure 1) show very distinct loss of O<sub>3</sub> in the first 3.5–4 km 202  
from the summit craters. Very often, except for conditions 203  
with very low wind speeds, the plume from Mt. Etna’s 204



**Figure 1.** Measurements of ozone concentrations from diffusion tube sampling on Mt Etna in 2004. The upwind measurements are marked separately.

summit craters can be seen to remain in contact with the slope for quite some distance before it disperses freely in the free troposphere. We interpret the data such that O<sub>3</sub> depletion can be observed in this region but not further away (and below) the summit craters due to the plume no longer being in contact with the ground. The two crater rim points have a large uncertainty due to interference with SO<sub>2</sub> and should be treated with caution. See Figure S1 in the auxiliary material for a correlation plot of SO<sub>2</sub> and O<sub>3</sub>, clearly showing that the diffusion tubes were inside the volcanic plume.

[15] The O<sub>3</sub> measurements in 2009 are shown in Table 2. The location is indicated as either on the slope or at the crater rim of the South East (SE), the North East (NE) or the Central (CC) crater. On 24 July, measurements were performed at three different locations on the slope of the Central Crater, for locations b and c two distinct time periods with different O<sub>3</sub> concentrations could be identified. At location c this coincided with a clear change in wind direction, which might have affected the mixing of air masses. It is unclear what caused the two distinct periods at location b, but the 2nd time period at that location shows significantly lower aerosol concentrations. It is interesting to note that the period with lower aerosol concentration shows a higher O<sub>3</sub> loss; this might hint at O<sub>3</sub> loss being more efficient in more dilute plumes. The distance is given to the crater that the respective plume originated from and the transport time was calculated using locally measured wind speeds (Kestrel 4500, Nielsen Kellerman) which showed a very large variability which is reflected in the range of the processing times given. O<sub>3</sub> was logged every 10s and the

variability of the O<sub>3</sub> loss was very large, therefore we show the mean and the variability of the O<sub>3</sub> loss relative to background concentrations. The available aerosol concentrations are listed in Table 2 as well. Please note that above about N = 75 1/cm<sup>3</sup> coincidence losses occur, so that most in-plume samples are lower limits. This data clearly shows that the measurements were taken inside the volcanic plume.

### 3.3. Eyjafjallajökull

[16] Data collected during the 45 plume interceptions of the Eyjafjallajökull plume are shown in Table S2 in the auxiliary material. The plume transect time series for six examples of such encounters are presented in Figure 2. Peak O<sub>3</sub> loss ranged between 4 and 84% per transect, with a mean of 37% and one standard deviation of 21%. There was clear spatial overlap between the profiles of the O<sub>3</sub> loss traces and those of the SO<sub>2</sub> in concert with a volcanogenic mechanism for the observed O<sub>3</sub> depletion. This was augmented with a marked correlation between the peak O<sub>3</sub> loss per transect and the maximum values from the SO<sub>2</sub> sensor (see Figure S2 in the auxiliary material) across the profile. The presence of a volcanic plume in the region of depleted O<sub>3</sub> was further confirmed by nephelometric measurements of mineral ash, whose light scattering coefficient profiles mimicked closely those of the SO<sub>2</sub> sensor.

[17] The scatter in the data likely arises from variations in the plume composition at source and different ambient conditions during the transport of the plume. Furthermore, due to the prevailing anti-cyclonic meteorology in the North Atlantic at the time of measurement, the plume was often composed of mixed batches and filaments of different ages due to recirculation, leading to variability in this processing time. Variation in the chemical composition of the plume, as a function of plume age, shows no discernable trend.

[18] The volcanic plume was found to be spatially inhomogeneous, being usually filamentary and composed of a number of partially merged layers. Assessment of the age of plume filaments intercepted is non trivial in the extreme. For more details on our estimates of plume age, ranging 1–9 days, see the auxiliary material.

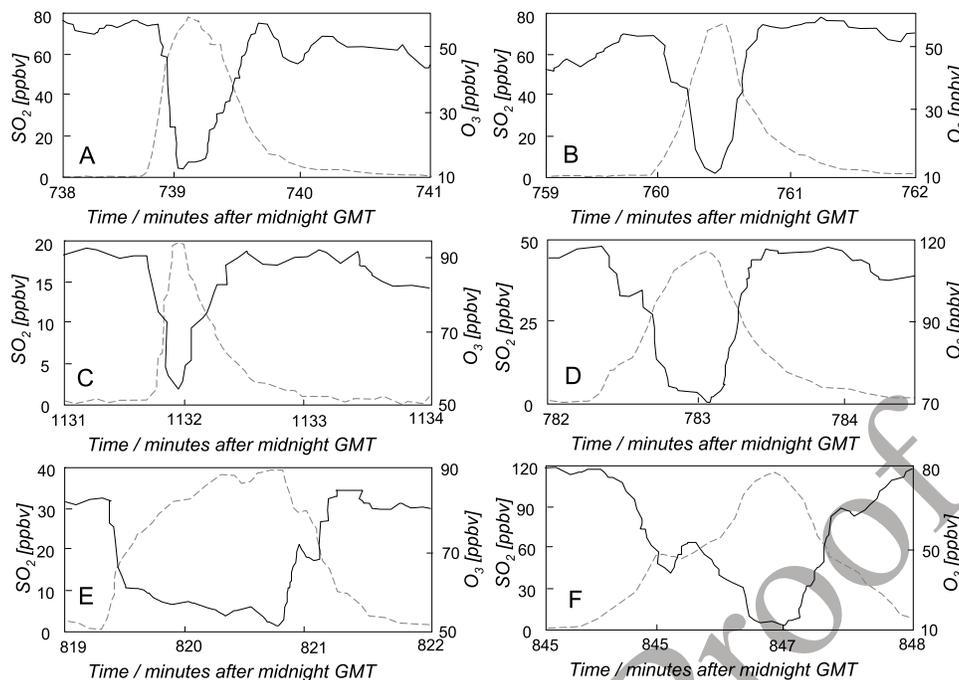
## 4. Discussion and Conclusions

[19] The data from the three very different volcanoes show that O<sub>3</sub> depletion is very widespread, starts within tens of seconds transport time from the crater and is sustained for

**Table 2.** Ground Based Measurements of O<sub>3</sub> Depletion in Vicinity of the Mt. Etna Summit Craters in July 2009<sup>a</sup>

Date	Location, Dist	Time	O <sub>3</sub> Loss	N [1/cm <sup>3</sup> ]	A [cm <sup>2</sup> /m <sup>3</sup> ]
16. July	background			17.5	6.3
09:53–10:17	SE slope, 1km CC	167–2000s	20 (2–38)%	562.2	22.7
11:51–12:35	NE crater, 2m NE	2–8s	24 (18–29)%	861.6	77.81
19. July				-	-
10:10–10:45	SE slope, 700m CC	108–125s	21 (–1–43)%	-	-
24. July	background			16.2	3.3
09:43–10:15	CC slope a, 770m CC	128–385s	22 (14–31)%	221.1	10.1
10:22–10:45	CC slope b, 590m CC	84–590s	33 (22–45)%	261.7	9.7
10:48–11:04	CC slope b, 590m CC	84–590s	40 (33–48)%	75.7	4.4
11:10–11:41	CC slope c, 526m CC	75–1052s	15 (8–21)%	146.2	10.0
11:43–11:56	CC slope c, 526m CC	88–526s	22 (16–27)%	-	-

<sup>a</sup>“Dist” is the distance to the crater from which the plume originated (CC – Central, NE–North East), “Time” is the transport time from the crater to the measurement site, N is the aerosol number concentration and A the aerosol surface area in the size range probed. For more explanation see text. All times are local times (GMT+2h).



**Figure 2.** Airborne measurements of 6 interceptions of the plume of Eyjafjallajökull in 2010. Ozone mixing ratios are shown with solid lines and SO<sub>2</sub> with dashed lines.

279 several days. The model calculations by *von Glasow* [2010]  
 280 show a very rapid and sustained depletion of O<sub>3</sub> compared  
 281 to regions outside of the plume which is consistent with our  
 282 measurements. In the model the O<sub>3</sub> depletion is mainly due  
 283 to catalytic bromine reactions in the volcanic plume. The  
 284 self-reaction of BrO causes 84% of the O<sub>3</sub> destruction in  
 285 the first hour and 90% of the O<sub>3</sub> destruction in the first 6 h  
 286 after plume release. Clearly chlorine chemistry would be  
 287 another candidate for rapid O<sub>3</sub> destruction but the available  
 288 evidence hints at a larger role of bromine (see discussion by  
 289 *von Glasow et al.* [2009]).

290 [20] Ozone has been reported to be taken up on silicate  
 291 dust and has been suggested to be responsible for O<sub>3</sub>  
 292 depletion in dust plumes [e.g., *de Reus et al.*, 2000]. Vol-  
 293 canic ash also contains large amounts of silicates so reactive  
 294 loss on ash might be an alternative or additional explanation  
 295 for the observed O<sub>3</sub> loss. The evaluation of laboratory data  
 296 by *Crowley et al.* [2010] recommends the following steady  
 297 state expression for the reaction of O<sub>3</sub> on mineral dust:  $\gamma =$   
 298  $1500 [\text{O}_3 (\text{cm}^{-3})]^{-0.7}$ , which for  $[\text{O}_3] = 50 \text{ ppbv}$  results in  $\gamma \approx$   
 299  $5.1 \times 10^{-6}$  with a rather large uncertainty. It should also be  
 300 mentioned that  $\gamma$  is likely a function of time, depending on  
 301 the composition of the surface and ambient conditions such  
 302 as humidity.

303 [21] Assuming an upper limit for the heterogeneous loss  
 304 of O<sub>3</sub> of  $\gamma = 10^{-5}$  the reactive aerosol surface area in the  
 305 volcanic plumes that we sampled would have had to be on  
 306 the order of  $1.93 \times 10^5$ ,  $3.2 \times 10^3$  and  $130 \text{ cm}^2/\text{m}^3$  in order  
 307 to explain an O<sub>3</sub> lifetime of 1min, 1h and 1day, respectively  
 308 (using equation (1) of *Crowley et al.* [2010]). Not very much  
 309 data is available about aerosol surface areas in volcanic  
 310 plumes but at Mt. Etna in 2009 we measured total aerosol  
 311 surface areas of only 4–78  $\text{cm}^2/\text{m}^3$  (see Table 2). For  
 312 St. Augustine we estimated the aerosol surface area for the  
 313 day with the highest particle loading [see *Stith et al.*, 1978]

to be  $\approx 150 \text{ cm}^2/\text{m}^3$ , which suggests that even in the most  
 314 dense parts of the plume that were sampled the lifetime of  
 315 O<sub>3</sub> to heterogeneous loss is on the order of a 1 day. Also  
 316 there is no clear difference in the O<sub>3</sub> loss as function of  
 317 estimated particulate mass flux (see Table 1), suggesting a  
 318 very weak influence of ash, if this influence is present at all.  
 319 Obviously the most dense parts of the plume had not been  
 320 probed so one might argue that in the early phases of strong  
 321 explosive eruptions the conditions for strong heterogeneous  
 322 O<sub>3</sub> loss might be given. As the dilution ratio in these plumes  
 323 is very large (one can make rough estimates from the change  
 324 in the SO<sub>2</sub> mixing ratio which near the vent is often several  
 325 ten percent but only on the order of a few hundred ppbv  
 326 hours to days downwind, see our data), ambient O<sub>3</sub> keeps  
 327 being mixed into the volcanic plume so in order to explain  
 328 sustained strong O<sub>3</sub> depletion hours and days downwind, O<sub>3</sub>  
 329 destruction must be ongoing. The surface areas required for  
 330 such a strong heterogeneous loss are not available, as  
 331 aerosol are also subject to very strong dilution and sedi-  
 332 mentation. Therefore we do not regard reactions on ash  
 333 aerosol as significant contributor to sustained O<sub>3</sub> depletion  
 334 in volcanic plumes.  
 335

[22] It is very likely that ash is being processed in volcanic  
 336 plumes, for example by exposure to high sulphuric acid  
 337 concentrations. Literature data suggests that an upper limit  
 338 for the accommodation coefficient for the uptake of O<sub>3</sub> on  
 339 sulphate particles is  $\alpha = 10^{-6}$  but likely much smaller  
 340 [*Sander et al.*, 2006] therefore our conclusion about the lack  
 341 of importance of heterogeneous loss of O<sub>3</sub> remains  
 342 unchanged.  
 343

[23] Based on this we regard the most likely cause for the  
 344 observed rapid and sustained O<sub>3</sub> loss to be catalytic reac-  
 345 tions with halogen, mainly bromine, radicals. This is con-  
 346 sistent with observations of BrO both in the vicinity of  
 347 volcanic craters and several days downwind from the vol-  
 348

349 cano from satellites. The main features of the measurements  
 350 are reproduced by the model by von Glasow [2010] indi-  
 351 cating that our general understanding of O<sub>3</sub> chemistry in  
 352 volcanic plumes as implemented in the model is realistic.

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