Ozone depletion in tropospheric volcanic plumes

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We measured ozone (O3) concentrations in the atmospheric plumes of the volcanoes St. Augustine (1976), Mt. Etna (2004, 2009) and Eyjafjallajökull (2010) and found O3 to be strongly depleted compared to the background at each volcano. At Mt. Etna O3 was depleted within tens of seconds from the crater, the age of the St. Augustine plume was on the order of hours, whereas the O3 destruction in the plume of Eyjafjallajökull was maintained in 1–9 day old plumes. The most likely cause for this O3 destruction are catalytic bromine reactions as suggested by a model that manages to reproduce the very early destruction of O3 but also shows that O3 destruction is ongoing for several days. Given the observed rapid and sustained destruction of O3, heterogeneous loss of O3 on ash is unlikely to be important.


1. Introduction

Volcanoes have long been recognised as major sources for gases and particles for the atmosphere. However for many years little attention was paid to their impact on the oxidation capacity of the troposphere. Bobrowski et al. [2003] showed the presence of very large amounts of bromine oxide (BrO) radicals in the plume of Soufrière Hills, Montserrat during quiescent degassing. Several other studies found BrO in the plumes of other passively degassing volcanoes [e.g., Oppenheimer et al., 2006; Bobrowski et al., 2007] and satellite observation also confirmed the presence of BrO in the plume of Kasatochi volcano after its explosive eruption in 2008 [Theys et al., 2009]. From other parts of the atmosphere we know that BrO mixing ratios of 1–10% of the values in volcanic plumes lead to very strong catalytic destruction of ozone (O3) [see, e.g., von Glasow and Crutzen, 2007], hence one would expect O3 depletion also to occur in volcanic plumes.

Very little data is available about O3 in volcanic plumes mainly due to logistical difficulties of access and cross-sensitivities of many O3 instruments to SO2. Broadband instruments measuring integrated UV absorption may have a positive interference with SO2, whereas wet-chemical methods as often used in balloon soundings have a negative cross-sensitivity on a mole-per-mole basis [Schenkel and Broder, 1982]. Hobbs et al. [1982] used an interference-free chemiluminescence technique and reported a 90% depletion of O3 in the plume of Mt. St. Helens compared to the background air, however they give very little details on this. Zerefos et al. [2006] found a strong O3 depletion in Mt. Etna’s plume over Greece, however they used a wet-chemical technique so the lack of O3 in their data might simply imply the presence of a volcanic SO2 layer. O3 depletion in stratospheric volcanic plumes has also been observed [e.g., Rose et al., 2006].

A number of modelling studies [Bobrowski et al., 2007; Roberts et al., 2009; von Glasow, 2010] has aimed at reproducing the observed halogen radicals in volcanic plumes and predict significant O3 destruction in the plume. The model used by von Glasow [2010] was initialised mainly based on observations at Mt. Etna. The results showed very strong O3 destruction in volcanic plumes for the whole duration of the model runs (3 days). More details about reactive chemistry in volcanic plumes can be found in the recent review by von Glasow et al. [2009]. In this paper we present data from a variety of instruments, volcanic settings and different campaigns that clearly show a strong O3 depletion in volcanic plumes.

2. Field Sites and Methods

2.1. St. Augustine (February 1976)

Airborne in situ O3 data were collected by the University of Washington (UW) Cloud and Aerosol research group during the January–February 1976 eruption of the St. Augustine Volcano, located in the lower Cook Inlet, southwest of Anchorage, Alaska.

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

Ozone measurements were made with a commercial chemiluminescence O3 analyzer (Monitor Labs model 8410A), which measures O3 by sensing light output from the reaction of O3 with ethylene. This technique has no known interferences with volcanic gasses but might over-read O3 by a few % at high humidities, so that our reported O3 losses are lower limits. It had a response time of less than 5s for 0 to 200 ppbv. The analyzer was calibrated with an UV-lamp-based calibrator (see Hegg et al. [1976] for more details).
operated by the Facility for Airborne Atmospheric Measurements (FAAM) made nine flights involving 45 transects of the Eyjafjallajökull plume, aged between 1 and 9 days old, as it was advected over the United Kingdom and northern France. The plume was generated via eruptive activity at Eyjafjallajökull, which commenced on 20 March. Lava extrusion through fissures resulted in Hawaiian style fire fountains, and generation of phreatomagmatic ash and gas plumes which rose up to 8 km. This event is publicly memorable for having resulted in an unprecedented closure of much of European airspace. Spatially, the plume, intersected during the measurements at altitudes between 4–8 km, was highly heterogeneous often consisting of multiple layers, suggestive of the recirculation within the persisting high pressure system, as observed by a number of satellite instruments.

12 SO2 and O3 were measured using Thermo Environmental Instruments Inc. Models 43 and 49C, respectively. The former is based on pulsed fluorescence and the latter on optical absorption. Contamination of the O3 signal by atmospheric SO2 is a known issue with such measurements; however in this case this does not apply as the 49C operates with dual cells: the reference and the sample, with the O3 being chemically scrubbed in the former. The difference between observed absorption in both cases is used to infer the O3 concentration. Therefore any interfering absorption from SO2 is cancelled out. The lowest detectable limit of O3 is 1 ppbv and the overall 2σ uncertainty is estimated at ±3 ppbv. The SO2 sensor is specified as having a lower than detection limit response to ambient ozone levels, ruling out cross-sensitivity in the opposite direction. The overall uncertainty for the SO2 instrument is 7–10%. The design of the sample inlet for the gas analysers is such that no significant aerosol reaches the instruments; this has been confirmed by inspection of the PTFE membrane filter fitted in the sample line immediately upstream. These data were augmented with simultaneously collected nephelometric proxies for plume mineral aerosol loading (from a separate inlet), derived from a three wavelength TSI Inc. 3563 unit. The inlet used with this instrument becomes increasingly inefficient for particles with diameter greater than approximately 5 μm. The largest source of error in data from both Thermo instruments is likely to result from rapid changes in gas concentration as the instruments’ integration times are 30 and 50 seconds for O3 and SO2, respectively.

3. Results

3.1. St. Augustine

13 A summary of the data from 27 plume interceptions is listed in Table 1 (all interceptions are shown in Table S1 in the auxiliary material). The O3 loss relative to the background values is on average 60% but has a very large variability (0–100%), which probably reflects differences in the plume composition on the different days but also different chemical processing due to different atmospheric conditions, e.g., mixing.

3.2. Etna

14 The diffusion tube measurements at Mt. Etna in 2004 (Figure 1) show very distinct loss of O3 in the first 3.5–4 km from the summit craters. Very often, except for conditions with very low wind speeds, the plume from Mt. Etna’s

### Table 1. Airborne Measurements of the O3 Depletion in the Plume of St. Augustine, 1976a

<table>
<thead>
<tr>
<th>Date</th>
<th>O3 Loss</th>
<th>State</th>
<th>Distance</th>
<th>Alt</th>
<th>Part. Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>09 Feb</td>
<td>20–50%</td>
<td>BE</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 Feb</td>
<td>67–87%</td>
<td></td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 Feb</td>
<td>0%</td>
<td>BE</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 Feb</td>
<td>44–89%</td>
<td>BE, ash</td>
<td>~24 km</td>
<td>2.1–2.4 km</td>
<td>60–3 × 10^5</td>
</tr>
<tr>
<td>14 Feb</td>
<td>78–100%</td>
<td>PE</td>
<td>28–56 km</td>
<td>1.8–2.4 km</td>
<td>30–90</td>
</tr>
<tr>
<td>16 Feb</td>
<td>52%</td>
<td>PE</td>
<td>2</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>18 Feb</td>
<td>23–67%</td>
<td>PE</td>
<td>~56 km</td>
<td>2.1–2.5</td>
<td>20–30</td>
</tr>
</tbody>
</table>

a“O3 loss” is relative depletion of O3 compared to background measurements, “Distance” is from the crater and “Alt” is the altitude above sea level. “State” is the eruption state: ME - major eruption, BE - between eruptions, PE - mostly post eruptive, ash - high ash loading and “Part. Flux” is the estimated flux (or range of fluxes, when more than one measurement was made) of particulate matter (in kg s⁻¹) measured on a given day after Stith et al. [1978].
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 O3 deple-
sions with different O3 concentrations could be identified. 

Central Crater, for locations b and c two distinct time per-
formed at three different locations on the slope of the 
location is indicated as either on the slope or at the 
travel time was calculated using locally measured wind 
transport time from the crater and is sustained for 
in the extreme. 

Table 2. Ground Based Measurements of O3 Depletion in Vicinity of the Mt. Etna Summit Craters in July 2009

<table>
<thead>
<tr>
<th>Date</th>
<th>Location, Dist</th>
<th>Time</th>
<th>O3 Loss</th>
<th>N [1/cm^3]</th>
<th>A [cm^2/m^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:53–10:17</td>
<td>SE slope, 1km CC</td>
<td></td>
<td></td>
<td>24 (18–29)%</td>
<td>562.2</td>
</tr>
<tr>
<td>11:51–12:35</td>
<td>NE crater, 2m NE</td>
<td>2–8s</td>
<td></td>
<td>861.6</td>
<td>77.81</td>
</tr>
<tr>
<td>19. July</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10:10–10:45</td>
<td>SE slope, 700m CC</td>
<td>108–125s</td>
<td>21 (=1–43)%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24. July</td>
<td>background</td>
<td></td>
<td>128–185s</td>
<td>22 (14–31)%</td>
<td>221.1</td>
</tr>
<tr>
<td>10:22–10:45</td>
<td>CC slope b, 590m CC</td>
<td>84–590s</td>
<td>33 (22–45)%</td>
<td>261.7</td>
<td>9.7</td>
</tr>
<tr>
<td>10:48–11:04</td>
<td>CC slope b, 590m CC</td>
<td>84–590s</td>
<td>40 (33–48)%</td>
<td>75.7</td>
<td>4.4</td>
</tr>
<tr>
<td>11:10–11:41</td>
<td>CC slope c, 526m CC</td>
<td>75–1052s</td>
<td>15 (8–21)%</td>
<td>146.2</td>
<td>10.0</td>
</tr>
<tr>
<td>11:43–11:56</td>
<td>CC slope c, 526m CC</td>
<td>88–526s</td>
<td>22 (16–27)%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

"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).
several days. The model calculations by von Glasow [2010] show a very rapid and sustained depletion of O3 compared to regions outside of the plume which is consistent with our measurements. In the model the O3 depletion is mainly due to catalytic bromine reactions in the volcanic plume. The self-reaction of BrO causes 84% of the O3 destruction in the first hour and 90% of the O3 destruction in the first 6 h after plume release. Clearly chlorine chemistry would be another candidate for rapid O3 destruction but the available evidence hints at a larger role of bromine (see discussion by von Glasow et al. [2009]).

Ozone has been reported to be taken up on silicate dust and has been suggested to be responsible for O3 depletion in dust plumes [e.g., de Reus et al., 2000]. Volcanic ash also contains large amounts of silicates so reactive loss on ash might be an alternative or additional explanation for the observed O3 loss. The evaluation of laboratory data by Crowley et al. [2010] recommends the following steady state expression for the reaction of O3 on mineral dust: 

\[ g = 1500 \left[ O_3 \, (cm^{-3}) \right]^{-0.7}, \]  

which for \([O_3] = 50\, \text{ppbv}\) results in \(g \approx 5.1 \times 10^{-6}\) with a rather large uncertainty. It should also be mentioned that \(g\) is likely a function of time, depending on the composition of the surface and ambient conditions such as humidity.

Assuming an upper limit for the heterogeneous loss of O3 of \(\gamma = 10^{-5}\) the reactive aerosol surface area in the volcanic plumes that we sampled would have had to be on the order of \(1.93 \times 10^5, 3.2 \times 10^5\) and \(130\, \text{cm}^2/\text{m}^3\) in order to explain an O3 lifetime of 1min, 1h and 1day, respectively (using equation (1) of Crowley et al. [2010]). Not very much data is available about aerosol surface areas in volcanic plumes but at Mt. Etna in 2009 we measured total aerosol surface areas of only \(4-78\, \text{cm}^2/\text{m}^3\) (see Table 2). For St. Augustine we estimated the aerosol surface area for the 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 dense parts of the plume that were sampled the lifetime of O3 to heterogeneous loss is on the order of a 1 day. Also there is no clear difference in the O3 loss as function of estimated particulate mass flux (see Table 1), suggesting a very weak influence of ash, if this influence is present at all. Obviously the most dense parts of the plume had not been probed so one might argue that in the early phases of strong explosive eruptions the conditions for strong heterogeneous O3 loss might be given. As the dilution ratio in these plumes is very large (one can make rough estimates from the change in the SO2 mixing ratio which near the vent is often several ten percent but only on the order of a few hundred ppbv hours to days downwind, see our data), ambient O3 keeps being mixed into the volcanic plume so in order to explain sustained strong O3 depletion hours and days downwind, O3 destruction must be ongoing. The surface areas required for such a strong heterogeneous loss are not available, as aerosol are also subject to very strong dilution and sedimentation. Therefore we do not regard reactions on ash aerosol as significant contributor to sustained O3 depletion in volcanic plumes.

It is very likely that ash is being processed in volcanic plumes, for example by exposure to high sulphuric acid concentrations. Literature data suggests that an upper limit for the accommodation coefficient for the uptake of O3 on sulphate particles is \(\alpha = 10^{-6}\) but likely much smaller [Sander et al., 2006] therefore our conclusion about the lack of importance of heterogeneous loss of O3 remains unchanged.

Based on this we regard the most likely cause for the observed rapid and sustained O3 loss to be catalytic reactions with halogen, mainly bromine, radicals. This is consistent with observations of BrO both in the vicinity of volcanic craters and several days downwind from the vol-

Figure 2. Airborne measurements of 6 interceptions of the plume of Eyjafjallajökull in 2010. Ozone mixing ratios are shown with solid lines and SO2 with dashed lines.
canoe from satellites. The main features of the measurements are reproduced by the model by von Glasow [2010] indicating that our general understanding of O3 chemistry in volcanic plumes as implemented in the model is realistic.

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