Halogen emissions from a small volcanic eruption: Modeling the peak concentrations, dispersion, and volcanically induced ozone loss in the stratosphere

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Received 19 May 2006; revised 7 July 2006; accepted 1 September 2006; published 12 October 2006.

[1] Aircraft measurements in the Hekla, Iceland volcanic plume in February 2000 revealed large quantities of hydrogen halides within the stratosphere correlated to volcanic SO_2. Investigation of the longer-term stratospheric impact of these emissions, using the 3D chemical transport model, SLIMCAT suggests that volcanic enhancements of H_2O and HNO_3 increased $HNO_3 \cdot 3H_2O$ particle availability within the plume. These particles activated volcanic HCl and HBr, enhancing model plume concentrations of ClO_x (20 ppb) and BrO_x (50 ppt). Model O_3 concentrations decreased to near-zero in places, and plume average O_3 remained 30% lower after two weeks. Reductions in the model O_3 column reduced UV shielding by 15% for 2 days. Plume incorporation into the winter polar vortex after 1 March elevated model vortex Cl_y and Br_y by 0.15 ppb and 7 ppt respectively, and doubled vortex ClO_x and BrO. Model results agree quantitatively with the observations made by the DC-8 aircraft. **Citation:** Millard, G. A., T. A. Mather, D. M. Pyle, W. I. Rose, and B. Thornton (2006), Halogen emissions from a small volcanic eruption: Modeling the peak concentrations, dispersion, and volcanically induced ozone loss in the stratosphere, *Geophys. Res. Lett.*, *33*, L19815, doi:10.1029/2006GL026959.

1. Introduction

[2] Small-scale explosive volcanic eruptions (10^{10}–10^{11} kg; Volcanic explosivity index 3) are relatively frequent, with about 3–4 each year [*Pyle*, 1995]. The eruption plumes from ~75% of these eruptions will reach altitudes >12 km [*Pyle et al.*, 1996], and approximately 30% will occur at latitudes higher than 40°, where tropopause altitudes lie at 10–12 km. Thus, high latitude VEI 3 eruptions may have a marked stratospheric impact, as demonstrated by the dominance of volcanic SO_2 in the lower stratosphere over anthropogenic SO_2 [*Graf et al.*, 1997]. Tropical eruptions need to be larger to show a similar impact; both because of the greater tropopause heights, and the greater water vapor content in the lower troposphere at tropical latitudes, which enhance removal of soluble acid gases. Atmospheric SO_2 is oxidized to sulfate aerosol, with the potential to change lower stratosphere dynamics [*Robock*, 2000] and catalyze halogen activation leading to stratospheric O_3 destruction [e.g., *Rosenfield et al.*, 1997].

[3] Volcanic emissions are typically dominated by water vapor, CO_2 and SO_2, with lesser quantities of H_2S, H_2 and CO. Volcanic emissions also often include halogen-bearing species including HF (0–1.2 mol%), HCl (0–1.7 mol%) and HBr (0–0.017 mol%) [*Symonds et al.*, 1994; *Bureau et al.*, 2000; *Aiuppa et al.*, 2005]. The molar composition of volcanic emissions varies between volcanoes, with the amount of hydrogen halide degassing often dependent on tectonic setting, volcano type and volcanic activity [e.g., *Gerlach*, 2004].

[4] Halogen emissions are extremely important to atmospheric chemistry due to their potential to destroy O_3 [*World Meteorological Organization*, 2003, and references therein]. Previous studies have implicated volcanic emissions in O_3 destruction by increasing the particle surfaces available for heterogeneous chemistry. It has been assumed that volcanic emissions are a trivial source of stratospheric ozone-depleting halogen compounds due to their scavenging in the troposphere [*Tabazadeh and Turco*, 1993]. A reduced impact on stratospheric O_3 in the future, due to reduction in global emissions of CFCs and HFCs brought about by legislation such as the Montreal Protocol [e.g., *Tie and Brasseur*, 1995; *Roscoe*, 2001], has also been suggested. Measurements of the volcanic plume of Hekla, Iceland, however, revealed that large quantities of volcanic halogens penetrated into the stratosphere [*Rose et al.*, 2006]. The dramatic enhancements of HCl, HF and HBr observed in the Hekla plume confirm that approximately 75% of the emitted volcanic HCl entered the stratosphere, and this was still present within the plume 35 hours after eruption [*Hunton et al.*, 2005; *Rose et al.*, 2006].

2. The Hekla Eruption 26 February 2000

[5] Historically, Iceland is one of the most active volcanic regions on the Earth, with several vigorous eruptions each decade. Ash falls from Icelandic eruptions are notably F-rich [*Oskarsson*, 1980]. Limited data suggest that hydrogen halides comprise 0.5–1 mole% of Icelandic volcanic gases [*Rose et al.*, 2006; *Thordarson et al.*, 1996; *Moune et al.*, 2006].

[6] The 2000 eruption of Hekla volcano in southern Iceland began at about 1815 UT on 26 February, with a brief (3–4 hr) explosive phase generating a volcanic cloud which reached 10–12 km a.s.l (VEI 3) and deposited ~10^7 m^3 (c. 10^{10} kg) of tephra across northern Iceland [*Rose et al.*, 2003]. The stratospheric volcanic plume from

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0094-8276/06/2006GL026959$05.00

this eruption was intercepted on several occasions by an instrumented NASA DC-8 aircraft [*Hunton et al.*, 2005; *Rose et al.*, 2006], revealing high plume HCl (>80 ppb) and HF(>60 ppb) concentrations. Modeling studies diagnosed volcanic enhancement of ClO_x concentrations to between 2 and 14 ppb and complete O_3 destruction within the plume within the first 35 hours in agreement with O_3 measurements [*Rose et al.*, 2006]. The increases in halogen gas concentrations seen in the Hekla plume represent a significant perturbation to stratospheric chemistry and halogen gases at these levels have seldom been modeled in the stratosphere. It is therefore important to investigate the evolution of the plume and diagnose the timescale over which these concentrations remain high.

[7] The DC-8 also measured increased concentrations of water vapor, HNO_3 and inorganic nitrogen during the plume interception. These were found to increase HNO_3:$3H_2O$ (NAT) and ice polar stratospheric cloud (PSC) threshold temperatures substantially over the first 35 hours [*Rose et al.*, 2006]. To test if this result remains true when plume dilution is included, we extend previous studies of the evolution of the Hekla plume chemistry, which ran on short timescales and neglected plume dilution, by using a 3D chemical transport model to investigate the impacts of both mixing and chemical evolution on plume composition for two weeks following the eruption.

3. Global Chemical Transport Model Setup

[8] SLIMCAT has a proven ability to model stratospheric composition over a wide range of conditions [e.g., *Chipperfield*, 1999]. Thus far SLIMCAT has not been used to study the dispersion and chemistry of volcanic plumes. The SLIMCAT model includes a comprehensive stratospheric chemistry scheme with reaction rates taken from *Sander et al.* [2003] and includes the formation of PSCs dependent on model temperatures and concentrations of water vapor, nitric acid and sulfuric acid. A long duration integration, started in 1991 [*Chipperfield*, 1999], was continued to cover the 1999/2000 Arctic winter as part of the THird European Stratospheric Experiment on Ozone (THESEO). Reinitialization from a long duration experiment provides realistic tracer distributions from the start of the run. The model was reinitialized for this study at a high resolution of 1.25° latitude by 1.25° longitude on 26 February 2000 on 10 isentropic surfaces spanning the potential temperature surfaces 330 to 2480K. The model was forced with 2.5° by 2.5° resolution, 6 hourly meteorological analyses from the European Centre for Medium Range Weather Forecasts (ECMWF).

[9] The Hekla eruption was simulated by injection of volcanic gases at and below 11.5 km between 18:15 and 22:00 UT; and at 10 km or below until 23:00 UT 26 February 2000, in accordance with radar measurements of plume top heights during the eruption [*Lacasse et al.*, 2004]. The main gases from Hekla were introduced in SLIMCAT at one grid point (64°N, 341°E) below the volcanic plume cloud top height (lowest 2 levels, decreasing to lowest level after 20:00 UT 26 February 2006) for the duration of the eruption: H_2O (6 ppm), SO_2 (1.2 ppm), H_2SO_4 (70.4 ppb), HF (60 ppb), HCl (45 ppb), CO (20 ppb), $ClONO_2$ (8 ppb), HNO_3 (4 ppb) and HBr (800 ppt), as in work by *Rose et al.* [2006]. A passive SO_2 tracer, assumed not to undergo chemical reaction, was added to SLIMCAT so that its concentration could be used to diagnose plume dilution. SO_2 oxidation is slow in the dry stratosphere, with only 3% oxidized within the first 35 hours, and is neglected here [*Rose et al.*, 2003]. The most significant impact of neglecting SO_2 oxidation will be a preservation of the HO_x reservoir [*Bekki*, 1995].

[10] Uncertainty exists over the form of volcanic NO_y emissions. NO, NO_2 and HNO_3 have previously been measured associated with both explosive and passive volcanic plumes. These species are thought to be produced due to the elevated temperatures associated with volcanism and lightning within ashy plumes [*Mather et al.*, 2004]. *Gerlach* [2004] showed that high-temperature mixing of air with volcanic gas could convert significant quantities of halogens to their oxidized forms (ClO, BrO). We may therefore expect some of the Hekla NO_x to react with activated volcanic chlorine to form $ClONO_2$ by the time the plume enters the stratosphere. For this reason, the total measured NO_y and HNO_3 onboard the DC-8 is distributed between the measured HNO_3 and $ClONO_2$, in a molar ratio of 1:2, as the Hekla source species supplied to the model on entry to the stratosphere. The integration was continued until 13 March 2000, by this date, volcanic source gases in the model had been diluted to <2% of their original concentrations.

4. Results and Discussion

4.1. Modeling Plume Residence Time and Dispersion

[11] The Arctic polar vortex became unusually cold and strong in the lower stratosphere from January 2000 [*Manney and Sabutis*, 2000], potentially reducing meridional mixing at 350 K potential temperature during the period under investigation, and we refer to air polewards of 70°N Potential Vorticity (PV) equivalent latitude as the polar vortex.

[12] The geopotential altitude range of the eruption column is such that volcanic source gases are injected into the stratosphere up to 350 K potential temperature at 65°N PV equivalent latitude, outside the lowermost stratospheric polar vortex. Plume evolution is strongly dependent on entry point to the stratosphere due to vertical and meridional wind shear. Less plume stretching and dilution is experienced with a more northerly entry point as wind velocities are lower towards the pole at this time. The vertical emplacement level also affects plume dispersal as stronger northerly wind speeds at 335 K, compared to 350K, transport the plume further into the 'quiet zone' (with wind speeds 5–10 ms^{-1}) and inhibit plume dilution.

[13] Both modeled plume position and column SO_2 abundance agree well with TOMS satellite data on 28 February (Figure 1). As the plume spreads, average SO_2 model concentrations within the 10 ppb SO_2 contour (defining the outer edge of the plume) rapidly reduce from 450 ppb at 00:00 UT 27 February to less than 100 ppb 2 days later. The dilution has a time constant of ~1 day (Figure 2), consistent with dominant zonal mixing along the flanks of the plume.

[14] The plume is stretched rapidly across the longitudes 30°W and 120°E and on the 29 February the most easterly

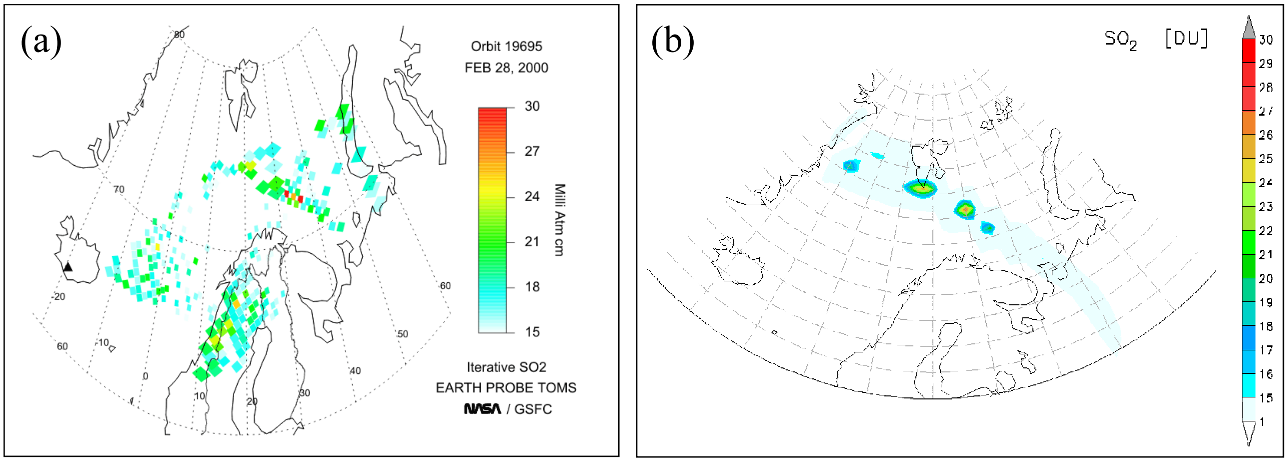

Figure 1. Hekla source gases from (a) TOMS SO_2 satellite data (28 February 2000) and (b) SLIMCAT SO_2 column (28 February 2000).

plume is folded southwards towards the Caspian Sea around a ridge of lower latitude air. The plume is incorporated into the edge of the polar vortex (defined here by 70°N PV equivalent latitude) on 1 March where it continues mixing and stretching within the edge of the polar vortex.

[15] Elevated SO_2 concentrations detected by the DC-8 interception within the polar vortex on the 9 and 15 March demonstrate that inclusion of plume gases enhanced vortex average SO_2 concentrations to between 1.5 and 3.45 ppb (enhanced by 10–30 times background levels), in good agreement with the vortex average SO_2 calculated by SLIMCAT (between 2.5 and 3.5 ppb at these altitudes, Figure 3).

[16] The closest interception between the plume remnant and the DC-8 is on the 13 March where plume SO_2 increases to 13.7 ppb. SLIMCAT does not accurately represent the interception point but does capture filament SO_2 concentrations of up to 5 ppb within ~450 km of the

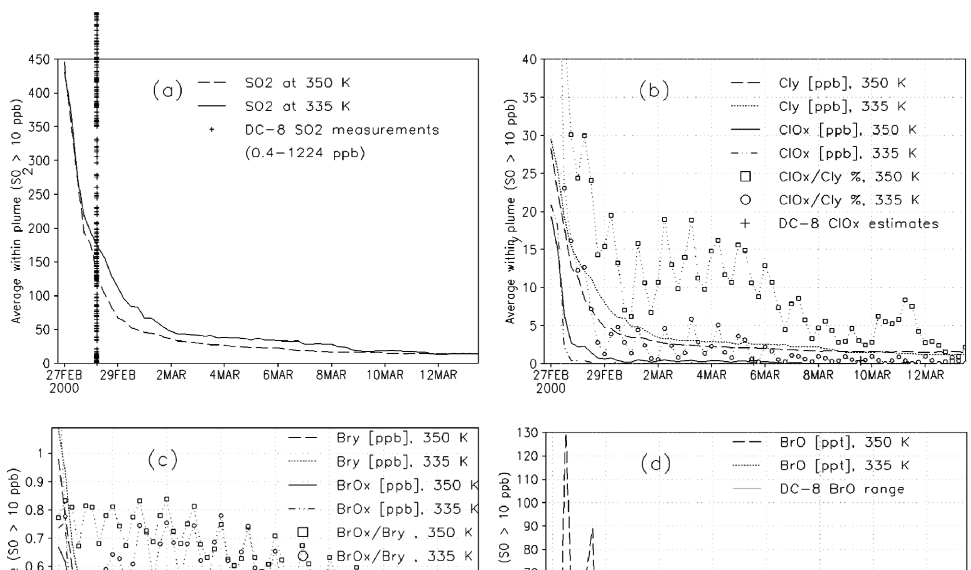

Figure 2. Average tracer concentrations within the volcanic plume, defined as $SO_2 \geq 10$ ppb, of (a) SO_2, (b) total inorganic chlorine, Cl_y, and activated chlorine, ClO_x, where $Cl_y = HCl + ClONO_2 + Cl + ClO + (2{*}Cl_2O_2) + OClO + HOCl$, and $ClO_x = Cl + ClO + (2{*}Cl_2O_2)$ (c) total inorganic bromine, Br_y, and active bromine BrO_x where $Br_y = HBr + BrONO_2 + Br + BrO + HOBr$, and $BrO_x = Br + BrO + BrCl$ (d) BrO. DC-8 measurements (at 310 K potential temperature), discussed by *Hunton et al.* [2005] and *Rose et al.* [2006] are also shown.

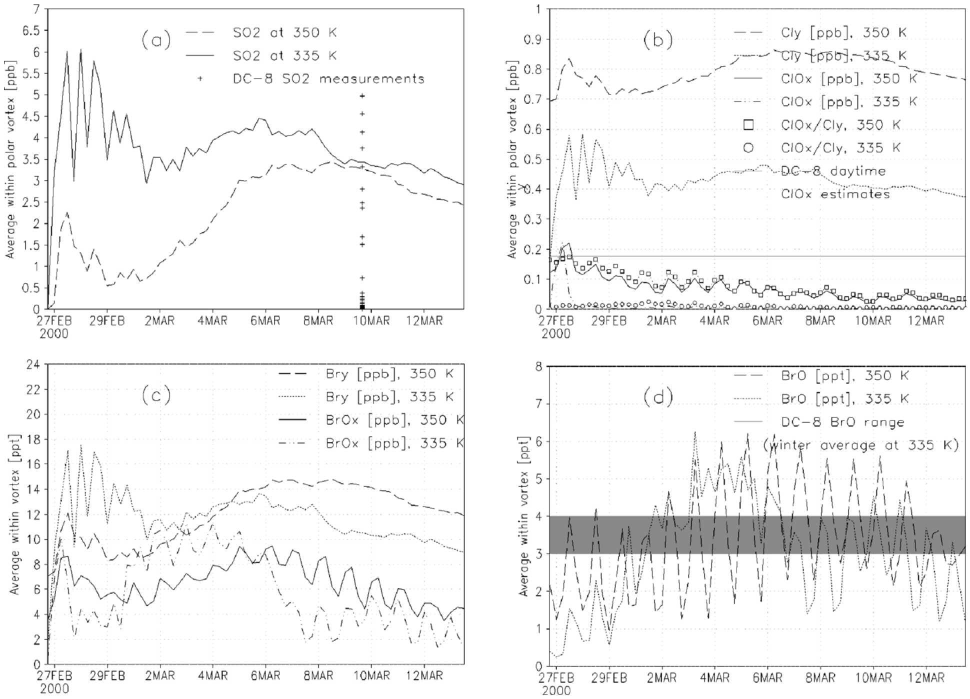

Figure 3. Average tracer concentrations within the lowermost polar vortex (poleward of 70° N PV equivalent latitude) of (a) SO_2 and DC-8 measurements of SO_2 inside the vortex, 9 March, (b) total inorganic chlorine, Cl_y, and activated chlorine, ClO_x, where $Cl_y = HCl + ClONO_2 + Cl + ClO + (2{*}Cl_2O_2) + OClO + HOCl$, and $ClO_x = Cl + ClO + (2{*}Cl_2O_2)$, measured entire winter daytime ClO_x at DC-8 altitudes is also shown (c) total inorganic bromine, Br_y, and active bromine BrO_x where $Br_y = HBr + BrONO_2 + Br + BrO + HOBr$, and $BrO_x = Br + BrO + BrCl$ (d) BrO and entire winter DC-8 estimated BrO at 335K is shown [*Thornton et al.*, 2003].

interception point. DC-8 measurements indicate that stratospheric plume filaments are still present with SO_2 concentrations greater than 13.7 ppb more than 2 weeks after the eruption. These are very fine-scale structures, with diameters smaller than ~210 km on 13 March, containing peak SO_2 concentrations >1 ppb. Even at the relatively high horizontal resolution of 1.25° by 1.25°, the model is limited to calculations within 140 km by 24 km boxes at these latitudes therefore peak concentrations within the plume are reduced. Unfortunately the complex chemistry required to model the evolution of species within the plume inhibits higher resolution modeling. Thus comparison of SLIMCAT model tracer concentrations to DC-8 measurements will be limited to peak and vortex average values during flights in March.

4.2. Volcanically Induced Polar Stratospheric Clouds (PSCs)

[17] Volcanic enhancement of HNO_3 and stratospheric water vapor increases the equilibrium formation temperature for NAT within the plume to 204 K at 00:00UT 27 February, reducing to 200 K by 1 March, compared to ~199K at background concentrations of HNO_3 and H_2O. Large surface areas of volcanically induced NAT PSCs are available from eruption to 29 February. Smaller NAT surface areas are predicted on 1 March and 2–4 March. Thereafter temperatures are too warm for NAT existence.

[18] In contrast to the box model results [*Rose et al.*, 2006], equilibrium formation temperatures for ice particles within the model are not raised sufficiently for ice formation due to rapid plume dilution before entry to the stratospheric cold pool above Scandinavia on 28 February. This modeled dilution may be more rapid than reality, as satellite evidence from *Rose et al.* [2003] diagnoses of the presence of ice within the plume until 28 February, suggesting the major aerosol component of the plume was either ice or ice-coated ash particles. Given these observations of ice in the plume, we would expect higher concentrations of ClO_x and BrO_x within the plume giving faster and more complete O_3 destruction than that predicted by the model.

[19] Vortex average equilibrium NAT threshold temperatures are also increased by 0.5K due to volcanic enhancement of polar vortex water vapor (7%) and nitric acid (12%).

4.3. Volcanic Hydrogen Halide Activation

[20] Our simulations demonstrate that total inorganic chlorine is dramatically enhanced within the plume with average concentrations peaking at nearly 30 ppb on 27 February followed by a rapid dilution to 1.5 ppb by 10 March at 10 km and 0.6 ppb at 11 km geopotential height. Plume model Cl_y concentrations are 40 times greater than background levels just after entering the stratosphere and a factor of three greater on 10 March. Unsurprisingly, the presence of volcanically induced PSCs leads to large increases in ClO_x concentrations of 20 ppb initially and between 0.2 and 0.5 ppb from the 29 February to 6 March, far in excess of levels usually observed at this altitude in the stratosphere. The loss of model PSCs after 4 March slowly

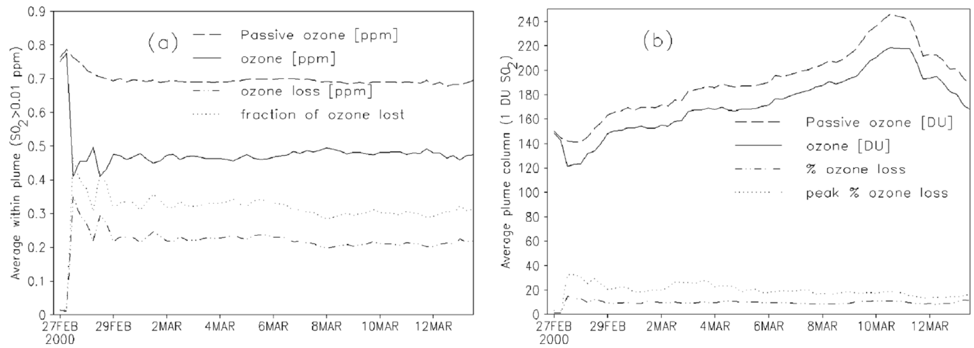

Figure 4. Ozone and ozone loss (a) at 350K potential temperature within the plume, defined by SO_2 > 10 ppb, and (b) in column, defined by column SO_2 > 1 DU. Passive ozone represents the ozone change due to transport alone. The percentage loss in ozone, relative to "passive ozone" is shown by "% ozone loss" averaged across the plume area. Peak values in column ozone loss are also shown.

reduces ClO_x concentrations to model background levels of 0.05 ppb by 13 March (Figure 2).

[21] Such large chlorine enhancements may be expected to make an impact on average vortex concentrations and general polar O_3 loss after plume incorporation in early March. Indeed, average polar vortex Cl_y is enhanced by ~50% to 0.8 ppb on 27 February, falling to 0.77 ppb on 13 March (Figure 3). Average polar vortex ClO_x is also enhanced by a factor of 3 initially, by the combination of increased inorganic Cl availability and increased heterogeneous activation. DC-8 based measurements of ClO_x in the plume on 5 and 9 March peaked at 50 ppt [*Rose et al.*, 2006], SLIMCAT vortex average ClO_x ranges between 40 to 80 ppt during this time.

[22] Volcanic chlorine is not the only threat to stratospheric O_3 as HBr is often degassed at molar concentrations between 0.1 to 1% of HCl [*Aiuppa et al.*, 2005; *Bureau et al.*, 2000] and is readily converted to reactive forms. Box modeling the Hekla plume with ~800 ppt HBr (40 times background) suggests that this concentration of Br would destroy background stratospheric O_3 within a couple of days, even in the absence of volcanic Cl [*Rose et al.*, 2006]. SLIMCAT BrO concentrations within the plume initially peaked at 130 ppt on 00:00UT 27 February, falling below 50 ppt on 4 March, in line with volcanic Br_y dilution. The short duration of peak values and small geographic scale may explain why volcanic BrO is not yet detected within volcanic plumes by satellite [*Afe et al.*, 2004]. The BrO upper limit during the DC-8 interception of the plume on 28 February is 15 ppt, SLIMCAT is in excellent agreement with night-time plume BrO concentration of 15 ppt rising to 50 ppt at midday. Vortex average BrO estimated from DC-8 observations over the whole winter [*Thornton et al.*, 2003] is in excellent agreement (Figure 3d) with SLIMCAT vortex average BrO which is increased above background concentrations by a factor of 2, after 1 March, to 3–6 ppt.

4.4. Volcanically Induced O_3 Loss

[23] Chemical O_3 loss can be difficult to diagnose in the lowermost stratosphere due to the long lifetime of O_3 and the large changes in O_3 concentration due to advection and mixing of polar air with low latitude, less O_3 rich air. SLIMCAT diagnoses dynamical changes to O_3 by inclusion of a chemically passive O_3 tracer, initialized at the start of the integration. The difference between this passive tracer and chemically active O_3 provides us with the chemical O_3 loss.

[24] The 3D model confirms earlier box model calculations of the dramatic O_3 loss inside the volcanic plume with near zero O_3 concentrations at some points. SLIMCAT diagnoses a plume average peak in volcanically-induced chemical O_3 loss of 0.3 ppb or 40% at 350K within the 10 ppb SO_2 contour, during the period of plume sunlight on the 28 February. Lower O_3 concentrations persisted at 350 and 335K within the plume beyond the end of the model run (over 2 weeks), although column O_3 was quickly replenished by changes in tropopause height (Figure 4). The impact of O_3 loss on surface UV levels may be investigated by looking at the average column O_3 loss across the horizontal area of the volcanic plume, where column SO_2 $\geq$ 1 Dobson unit (DU). Figure 4b shows that the volcanic eruption was responsible for a decrease of 20 DU in column O_3 in the first 2 days after eruption and increased to pre-eruption levels by 29 February. Hence, according to SLIMCAT simulations, surface UV shielding was reduced by 15% under the plume for this 2-day period. The limited vertical extent of volcanically-induced O_3 depletion allows fast O_3 column recovery by changes in tropopause heights bringing more O_3 rich air into the column above the volcanically perturbed layer. DC-8 observations confirm near complete O_3 depletion in regions of the plume on 28 February, and apparent O_3 depletion of over 100 ppb in the aged plume on 5 and 9 March [*Rose et al.*, 2006].

[25] The second period of volcanically-induced NAT PSC formation, between 2 and 4 March, did not lead to significant plume O_3 loss due to the much more dilute Cl_y and Br_y at this time. A volcanic eruption of this size has a limited impact on stratospheric O_3, however larger eruptions which penetrate further into the stratosphere may reduce column O_3 more severely, for a longer duration.

5. Conclusions

[26] Injection of large amounts of volcanic water and nitric acid into the lower stratosphere by the Hekla eruption increased the equilibrium threshold temperature for nitric acid trihydrate (NAT) particle formation, generating large surface areas for heterogeneous activation of the volcanic Cl and Br. Dilution within the model took place at a faster rate than diagnosed within the plume by DC-8 measurements,

yet the model still experienced significant O_3 loss within the lowermost stratosphere persisting for >2 weeks. The SLIMCAT model captures the near zero O_3 concentrations, and plume average O_3 loss approaching 50% at the DC-8 intercept altitudes. The O_3 column and hence surface UV shielding was reduced by 15% within the lateral extent of the plume for a period of two days. Larger eruptions that penetrate deeper into the stratosphere will produce a more severe reduction in surface UV shielding for a longer duration.

[27] The dispersal and lifetime of a volcanic plume is highly dependent on the local meteorology. As expected, medium to strong wind speeds rapidly reduce volcanic gas concentrations to lower levels, reducing the likelihood of volcanically induced polar stratospheric cloud (PSC) formation and O_3 loss. Earlier work showing volcanically induced enhancements of ClO_x and BrO_x of 20 ppb and 50 ppt is confirmed with inclusion of transport and mixing, however the duration of these peak concentrations is greatly reduced due to dilution.

[28] Previous studies of stratospheric chemistry after volcanic eruptions have diagnosed O_3 sensitivity to volcanic aerosol and have speculated that this sensitivity will fall after chlorofluorocarbon emissions have reduced. This work demonstrates that stratospheric O_3 is not only sensitive to volcanically induced aerosols, but is also sensitive to the flux of volcanic hydrogen halides.

[29] **Acknowledgments.** We thank Darin Toohey for DC-8 ClO_x and BrO measurements and valuable discussions. The financial support of the Leverhulme Trust and the Royal Society is gratefully acknowledged. NCAS, CAS and John Pyle are thanked for technical support.

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