Catastrophic Loss of Stratospheric Ozone in Dense Volcanic Clouds

MICHAEL PRATHER

Department of Geosciences, University of California, Irvine

Rapid, localized loss of ozone is predicted to occur in the mid-latitude and tropical stratosphere in the presence of very large concentrations of sulfate aerosols. Volcanic eruptions can increase the effective surface area of sulfuric acid so that heterogeneous reactions involving $ClONO_2$, and secondarily N_2O_5, are able to suppress NO_x abundances by more than a factor of 10 relative to gas phase chemistry. When NO_x levels fall below a threshold, e.g., 0.6 ppb at 24 km in mid-latitudes, the chlorine-catalyzed loss of O_3 proceeds at rates comparable to those during the formation of the Antarctic ozone hole, more than 50 ppb per day. If such losses occurred following the eruption of Mount Pinatubo in the most volcanically perturbed regions over the tropics and mid-latitudes, this model predicts that they are driven primarily by the suppression of NO_x below these critical levels. The increase in stratospheric chlorine since El Chichon has made Mount Pinatubo more than twice as effective in causing rapid O_3 loss. Overall global losses associated with a volcanic eruption are approximately linear in the amount of sulfate surface area, but depend critically on the rate of the $ClONO_2$-sulfate reaction.
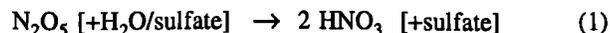
1. INTRODUCTION

Ever since laboratory measurements first showed that chemical reactions of stratospheric concern occur on sulfuric acid - water mixtures [*Tolbert et al.,* 1988; *Mozurkewich and Calvert,* 1988], photochemical models have been used to demonstrate that large increases in the stratospheric sulfate layer due to volcanic eruptions could lead to measurable ozone depletion by enhancing the chlorine-catalyzed destruction of ozone [*Hofmann and Solomon,* 1989]. Since then, further laboratory studies have confirmed that heterogeneous chemistry occurs on sulfate aerosols [*Van Doren et al.,* 1991; *Hanson and Ravishankara,* 1991; also J. A. Manion et al., Heterogeneous reaction of N_2O_5 and $ClONO_2$ on sulfuric acid surfaces representative of global stratospheric particulate, submitted to *Journal of Geophysical Reasearch,* 1992 (hereinafter Manion et al., submitted manuscript, 1992)]. Additional model studies continue to predict the importance of these reactions to stratospheric ozone [e.g., *Mather and Brune,* 1990; *World Meteorological Organization (WMO),* 1992] by affecting long-term trends due to the buildup of atmospheric chlorine [*Rodriguez et al.,* 1991], volcanic eruptions [*Brasseur et al.,* 1990], or projected aircraft emissions [*Weisenstein et al.,* 1991].

I show here the existence of a nonlinear, catastrophic (i.e., rapid) response in stratospheric photochemistry to the addition of sulfate aerosols. There exists a threshold, above which the odd-nitrogen (NO_y) chemistry shuts down, as shown previously for the case of multiple solutions [*Prather et al.,* 1979] or in the case when chlorine levels (Cl_y) globally exceed NO_y abundances [*Prather et al.,* 1984]. If the sulfate aerosol loading reaches these critical levels, as might have occurred in some regions during the months following a major volcanic eruption such as Mount Pinatubo in June 1991 [*McCormick,* 1992], then the chemistry shifts to a predominantly Cl_y plus HO_x (= OH + HO_2) system. Ozone loss rates become equivalent to those over springtime Antarctica when the ozone

hole is created, more than 50 ppb (1%) per day [e.g., *Schoeberl et al.,* 1989; *Solomon,* 1990]. In this case, however, such ozone losses are predicted to occur in the middle latitudes or even the tropics under bright sunlit conditions.

2. HETEROGENEOUS CHEMISTRY

The critical impact of sulfate layer chemistry, as noted by *Rodriguez et al.* [1991], is to move the odd-nitrogen species from NO_x (= NO + NO_2) into HNO_3 by two heterogeneous reactions:

$$N_2O_5 \text{ [+}H_2O/\text{sulfate]} \rightarrow 2 HNO_3 \text{ [+sulfate]} \qquad (1)$$

$$ClONO_2 \text{ [+}H_2O/\text{sulfate]} \rightarrow HNO_3 + HOCl \text{ [+sulfate]} \qquad (2)$$

The rate coefficient for each reaction (s^{-1}) is calculated as the product of the reaction probability (γ, dimensionless), the aerosol area (α, cm^2 cm^{-3} or cm^{-1}), and the mean speed of the gaseous species (cm s^{-1}) divided by 4. Reduction in the NO concentration leads indirectly to increases in ClO by changing the balance of HCl to ClO through the reduced efficiency of the reaction sequence,

$$ClO + NO \rightarrow Cl + NO_2 \qquad (3)$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (4)$$
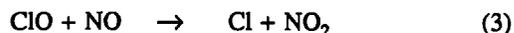
The photochemical model [*Prather and Jaffe,* 1990; *DeMore et al.,* 1990; *Prather,* 1992] is used to derive a steady state cycle of all chemical species over 24 hours. The primary case study shown here is for the mid-latitude, middle stratosphere: 24 km altitude (29 mbar) at 45°N in March. Results from the two limiting cases of gas phase only ($\gamma_1 = \gamma_2 = 0$) and the aerosol-saturated case ($\gamma_1 = 0.1$, $\gamma_2 = 0.01$, $\alpha = 1000 \times 10^{-8}$ cm^{-1}) are given in Table 1. The two limits demonstrate clearly the difference between the gas phase NO_x-dominated chemistry and the aerosol-saturated Cl_y-HO_x chemistry. The transition from gas phase to aerosol-saturated depends critically on the reaction probability of (2) and is examined in Figures 1-3. Release of ClO from the HCl reservoir (by reaction with OH) will be rapid, less than 20 days, once the HO_x levels rise in
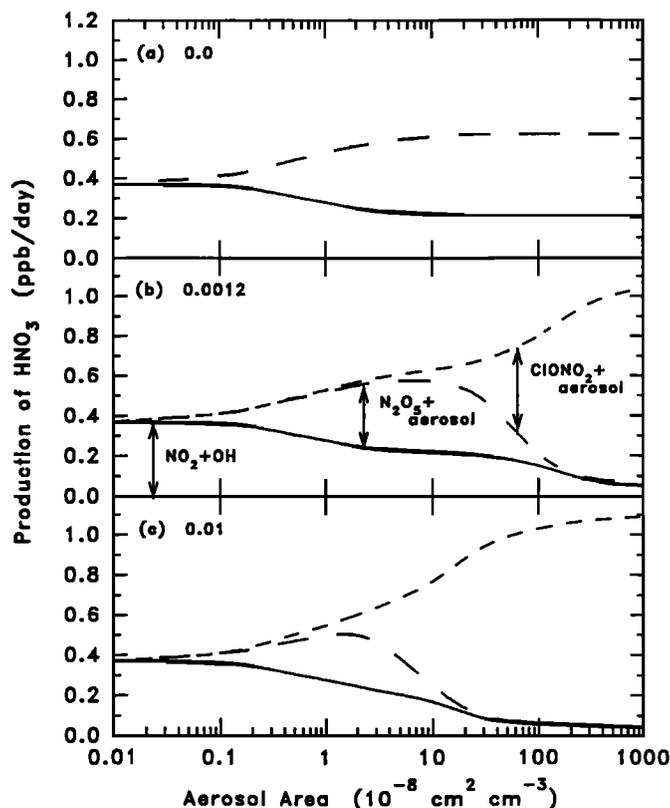
Fig. 1. Cumulative production rate of HNO_3 (parts per billion per day) as a function of aerosol surface area (α, 10^{-8} cm^2cm^{-3}) for the three reactions: NO_2+OH, N_2O_5+aerosol, $ClONO_2$+aerosol. Calculations apply to 45°N in March at 24 km altitude (see Table 1). The panels show results for different values for the reaction probability of $ClONO_2 + H_2O/H_2SO_4$: (a) $\gamma_2 = 0.0$, (b) $\gamma_2 = 0.0012$, (c) $\gamma_2 = 0.01$.

Fig. 2. (a) Net ozone loss (parts per billion per day) and (b) noontime NO_x (parts per billion) as a function of aerosol surface area (α, 10^{-8} cm^2cm^{-3}) for different γ_2. Calculations apply to 45°N in March at 24 km altitude (see Table 1). Also denoted are the loss rates typical during the formation of the Antarctic ozone hole, and the sulfate aerosol areas typical of background levels and after large volcanic eruptions, such as Mount Pinatubo. Net O_3 loss for $\gamma_2 = 0.0012$ with a 25% reduction in Cl_y (2.1 ppb) is shown in Figure 2a as a dotted line.

response to the reduced NO_x abundances. Therefore, the assumed steady state balance among NO_y and Cl_y species is readily achieved.

The relative importance of reactions (1) and (2) in producing HNO_3 is shown in Figure 1. For $\alpha < 0.1 \times 10^{-8}$ cm^{-1} the gas phase formation of HNO_3 dominates:

$$NO_2 + OH\ [+M] \quad \rightarrow \quad HNO_3\ [+M] \tag{5}$$

As the area increases, the pathway through reaction (1) becomes comparable to (5). Without reaction (2), as in Figure 1a, the impact of heterogeneous chemistry saturates for $\alpha > 10 \times 10^{-8}$ cm^{-1}. When reaction (2) is included with probability equal to 0.0012, as in Figure 1b, the reaction path through $ClONO_2$ quickly becomes the dominant source of HNO_3 (and HOCl as well). If the probability of reaction (2) is as large as 0.01 (Figure 1c) then it becomes important even at background levels of aerosols.

The abundance of NO_x is shown in Figure 2b for these same three cases. Even at background levels, NO_x is suppressed by a factor of 2 relative to the gas phase limit [e.g., *Mather and Brune,* 1990; *Rodriguez et al.,* 1991]. For large surface areas associated with volcanic eruptions [*Hofmann and Solomon,* 1989; *McCormick and Veiga,* 1992], locally NO_x mixing ratios can be reduced by more than a factor of 20. Measurements of NO_2 after Pinatubo show substantial reductions, greater than 20% [*Johnston et al.,* 1992], but these column integrals cannot resolve the perturbations within the volcanic layers. Under
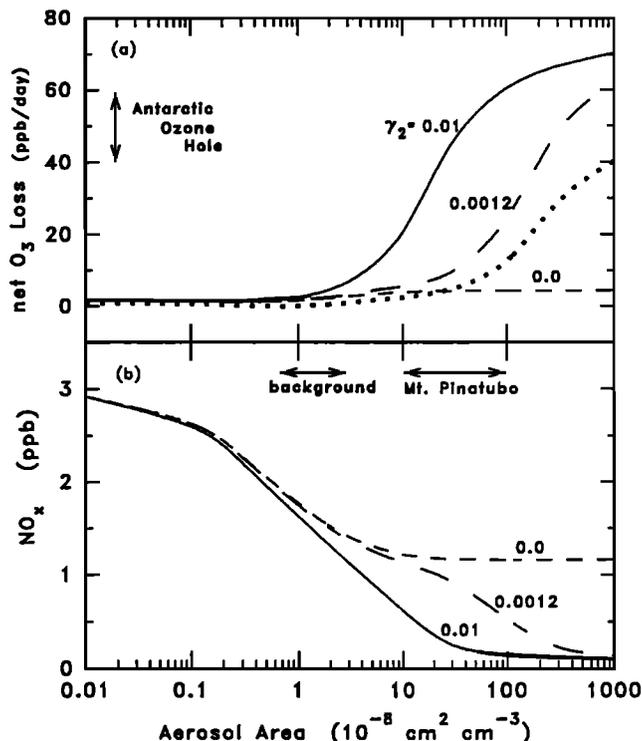
these conditions the reduction in NO_x depends critically on the reaction probability of (2). Reaction (1) alone cannot reduce the NO_x abundance below 1.2 ppb (at 24 km, 45°N in March) because the rate is essentially quadratic in NO_x densities (i.e., the formation of N_2O_5 is proportional to the product of NO_2 and NO_3). When NO_x is less than 1.2 ppb the formation of N_2O_5 overnight (and its subsequent reaction on sulfate aerosols) does not compete with the daylight photochemistry. With the addition of reaction (2), the enhancement of aerosol surface area can further suppress NO_x (i.e., formation of $ClONO_2$ is linear in the NO_x abundance, being proportional to the product of ClO and NO_2) to a new asymptotic value of 0.1 ppb.

3. RAPID OZONE LOSS

Net loss rates for O_3 as functions of α and γ_2 are shown in Figure 2a. At 24 km, 45°N in March for gas phase chemistry, the ozone is almost in balance: production of 25.4 ppb/day is offset by losses of 27.4 ppb/day (see Table 1). Ozone losses increase linearly at first with aerosols for areas greater than 1×10^{-8} cm^{-1} (background); this would be apparent if Figure 2a were plotted with a linear abscissa. The rate of increase with aerosol area depends sensitively on γ_2. For $\gamma_2 = 0.0$, the O_3 loss becomes constant for α between 10 and 30×10^{-8} cm^{-1} because NO_x no longer decreases. For $\gamma_2 = 0.01$, the O_3 loss asymptotes (for α between 100 and 300×10^{-8} cm^{-1}) at 70 ppb per day, equivalent to loss rates during formation of the

Antarctic ozone hole [*Schoeberl et al.*, 1989]. In the cases shown here, the ozone loss rate can be derived simply as a function, albeit a highly nonlinear function, of the NO_x abundance. Rapid ozone loss only begins when the noontime NO_x mixing ratios fall below 0.6 ppb, and Antarcticlike losses of greater than 50 ppb per day occur when NO_x levels reach 0.2 ppb. Cumulative loss rates due to the O_x, NO_x, HO_x, ClO_x, and BrO_x catalytic cycles (see definitions in Table 1) are shown in Figure 3 as a function of α for the case $\gamma_2 = 0.01$. For smaller γ_2 the asymptotic limit would shift to large α. Total losses under these conditions (24 km at 45°N in March) exceed 90 ppb per day as the area approaches 1000×10^{-8} cm^{-1}: the combined total of NO_x+HO_x loss remains approximately

TABLE 1. Limiting Cases of Gas Phase and Sulfate Aerosol Chemistry at 45°N, 24 km (219 K, 29 mbar)

Initial Concentration		
O_3,	ppm	4.5
H_2O,	ppm	4.0
H_2,	ppm	0.5
CH_4,	ppm	1.1
NO_y,	ppb	10.6
Cl_y,	ppb	2.8
Br_y,	ppt	15.

	Gas Phase Only $\gamma_1 = \gamma_2 = 0$ $\alpha = 0$	Aerosol-Saturated Case $\gamma_1 = 0.1$, $\gamma_2 = 0.01^*$ $\alpha = 1000 \times 10^{-8}$ cm^{-1}
Noontime Mixing Ratios		
OH, ppt	2.22	5.24
HO_2, ppt	10.9	25.0
NO, ppb	1.22	0.02
NO_2, ppb	1.70	0.08
N_2O_5, ppb	0.61	0.00
HNO_3, ppb	5.32	10.42
$ClONO_2$, ppb	0.93	0.07
HCl, ppb	1.76	0.44
HOCl, ppb	0.03	1.01
ClO, ppb	0.09	1.23
Cl, ppt	0.069	0.050
Production (24-hour Average Rates), ppb/day		
O_2 + hv (×2)	21.8	21.8
HO_2 + NO (×1)	3.6	0.2
O_x Loss, ppb/day		
O_3 + O (×2)	2.4	2.4
NO_x Loss, ppb/day		
NO_2 + O (×2)	14.3	0.5
NO_3 + hv (×2)	0.8	0.1
HO_x Loss, ppb/day		
HO_2 + O_3 (×1)	5.4	16.7
OH + O_3 (×1)	1.5	4.1
Cl_y + Br_y Loss, ppb/day		
ClO + O (×2)	2.4	38.7
Cl_2O_2 + hv (×2)	0.0	6.1
HOCl + hv (×1)	0.3	12.6
BrO + ClO (×2)	0.3	11.1
Net Production minus Loss, ppb/day		
O_3	-2.0	-70.3

* The large values for γ_2 and α are chosen here to illustrate the upper limit in the heterogeneous NO_y processing; the suppression of NO_x depends on their product. Note that $\gamma_2 = 0.01$ would apply to colder temperatures or to enhanced water vapor.
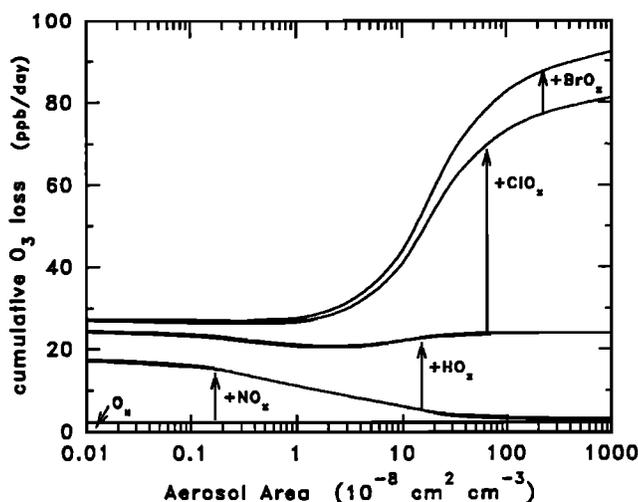
constant as the total of ClO_x+BrO_x loss increases by more than a factor of 10.

This potential for rapid ozone loss extends over much of the stratosphere. Beyond the example shown here, similar behavior with O_3 losses of 20 to 40 ppb per day extends down to 20 km altitude at 45°N. In the tropical stratosphere, the net O_3 tendency is largely positive (primary production by O_2 photodissociation greatly exceeds chemical losses). Nevertheless, the addition of rapid heterogeneous processing to the altitude range 24-28 km at 15°N in March can increase the ClO_x plus HO_x-catalyzed losses by as much as 40 ppb per day, with the net still remaining positive. At higher altitudes in the stratosphere, the effect of heterogeneous chemistry is more complex: the initial suppression of NO_x-catalyzed loss dominates and leads to reduced O_3 losses with increasing aerosol area; only at very high aerosol areas would NO_x levels fall below the critical threshold as described above. The maintenance of such large surface areas of sulfuric acid - water mixtures at higher altitudes and warmer temperatures is difficult and would require significantly greater sulfur and water abundances [e.g., *Hamill et al.*, 1988].

A question remains as to why this effect, the nonlinear suppression of NO_x followed by the catastrophic loss rate of O_3, has not been reported in previous studies on the subject of volcano-induced ozone loss. *Brasseur et al.* [1990] assumed large aerosol loadings, reaching 35×10^{-8} cm^{-1} at 24 km over the equator, and a value of $\gamma_2 = 0.0026$, which stops just short of the rapid losses shown in Figure 2a. However, their Figure 2 shows clearly that global ozone loss becomes sensitive to γ_2 rather than γ_1, reaching -25% (globally!) for $\gamma_2 = 1$. *Hofmann and Solomon* [1989] used γ_2 values of 0.0065 and α peak aerosol areas of about 40×10^{-8} cm^{-1}, less at 24 km. They predicted large increases in HOCl (as here) but did not report on the nonlinearity where the high ClO becomes a positive feedback in the NO_x cycles and the chlorine-catalyzed loss rapidly escalates. *Rodriguez et al.* [1991] considered only reaction (1) and would not have seen this phenomenon.

In the presence of such large aerosol content, what other modifications of the stratospheric environment might affect O_3 chemistry? For one, the enhanced scattering from the aerosols [*Michelangeli et al.*, 1989] will increase photolysis rates at the top of the cloud and reduce them near the bottom. Further, net radiative heating by the aerosols may also perturb the temperature [*Labitzke and McCormick*, 1992], and possibly lead to a change in the mean diabatic circulation (S. Kinne et al., Radiative impact of Pinatubo aerosols on tropical ozone, manuscript in preparation, 1992). These perturbations are too complex to analyze with this model. Their impacts on stratospheric O_3 may be important, but on a localized parcel scale they are likely to be small compared with the dramatic shift in the chlorine-catalyzed ozone loss discussed here.

4. LABORATORY AND ATMOSPHERIC CONSTRAINTS

The different laboratory measurements are in qualitative agreement regarding the sharp dependence of reaction (2) on the water content of the sulfuric acid - water mix, although absolute values for γ_2 vary by a factor of 2 [*Tolbert et al.*, 1988; *Hanson and Ravishankara*, 1991; also Manion et al., submitted manuscript, 1992]. A γ_2 of 0.01 or greater corresponds to extremely wet mixtures with less than 52% by weight of H_2SO_4. Such wet sulfuric acid droplets would occur in the lower-middle stratosphere only if temperatures dropped

Fig. 3. Cumulative O_3 loss (parts per billion per day) as a function of aerosol surface area (α, 10^{-8} $cm^2 cm^{-3}$) for different catalytic cycles with $\gamma_2 = 0.01$. Calculations apply to 45°N in March at 24 km altitude (see Table 1).

to 197 K or less (approaching the threshold for condensation of nitric acid - water mixtures [Hanson and Mauersberger, 1988]), or if water vapor were greatly enhanced. Values of γ_2 = 0.0012 correspond to 66%wt H_2SO_4 and stratospheric temperatures of about 210 K; while $\gamma_2 = 2\times10^{-4}$ (not shown in calculations above) is applicable to 75%wt solutions (about 224 K) and may be an effective rate for reaction (2) throughout much of the middle stratosphere.

The uncertainty in γ_2 from the laboratory data ($\pm50\%$) is matched by the uncertainty in averaging γ over a range of stratospheric temperatures. The exponential dependence of γ_2 on %wt H_2SO_4 and thus on temperature (i.e., a factor of 2 for each change of 5 K), makes the temperature history of an air parcel an extremely important factor in averaging the effective rate of reaction (2). The range in γ_1 from the laboratory data, 0.05 to 0.14, would not greatly affect these results because reaction (1) is ineffective at low levels of NO_x.

The available surface area for reactions (1) and (2) throughout the stratosphere in the form of liquid sulfuric acid aerosols is highly variable [Hofmann, 1990] and not easy to define [Thomason, 1991]. Background levels in the middle-lower stratosphere at mid-latitudes (i.e., the cleanest periods observed over the last decade) are about 1×10^{-8} cm^{-1}, with a range of at least a factor of 2. Several months after the eruption of El Chichon in 1983, surface areas in excess of 40×10^{-8} cm^{-1} were observed [Hofmann and Solomon, 1989], but values above 24 km were a factor of 8 less. Current estimates indicate that the sulfur injected by Mount Pinatubo (June 1991) exceeded that,of El Chichon by a factor of 2 to 3 [Bluth et al., 1992] and reached higher altitudes [McCormick and Veiga, 1992]. Early observations of aerosol optical extinction (proportional to the surface area of the larger particles) show large regions in the tropical stratosphere with $\alpha > 100\times10^{-8}$ cm^{-1} at altitudes near 24 km. It is likely that significant volumes of the tropical and mid-latitude stratosphere were exposed to such large effective surface areas of sulfuric acid droplets.

In summary, the uncertainty in laboratory measurements and stratospheric conditions suggest a range for γ_2 of 0.0001 to 0.0012 for the middle stratosphere, with larger values in the

lower stratosphere or where temperatures are much colder. If the effective γ_2 were of order 0.01 in the lower stratosphere, then this proposed mechanism should have been (but was apparently not) triggered by El Chichon [Hofmann and Solomon, 1989; Chandra and Stolarski, 1991]. If the averaged γ_2 were to exceed 0.002 in some regions, then Mount Pinatubo may have injected enough sulfur into the stratosphere for an unambiguous test.

5. IMPLICATIONS AND TESTS

The chlorine-catalyzed ozone loss predicted here for mid-latitudes is similar in magnitude to polar processes causing the Antarctic ozone hole, but is driven predominantly by the O+ClO and HOCl+hv cycles, rather than the Cl_2O_2 cycle. The loss is described here as catastrophic in that large, isolated parcels of perturbed air may experience measurable ozone loss, of order 1% per day, in the 2-3 weeks before they mix with the background stratosphere [Prather and Jaffe, 1990]. Such a property makes this type of O_3 loss more readily detectable than if the equivalent loss were spread globally over a season. Average global loss of ozone, on the other hand, will depend less on the details of rapid loss in these clouds and more critically on the rate of this heterogeneous reaction and its ability to suppress NO_x. Calculations of global ozone response to large volcanic injections must also include dynamical transports as in the global chemical transport models of Brasseur et al. [1990] and Rodriguez et al. [1991].

Hofmann and Solomon [1989] point out that the volcano-modulated O_3 loss they ascribe to El Chichon (however, see Chandra and Stolarski [1991]) might be much greater for large volcanic injections in the future when chlorine levels are greater. Pittock's [1965] observation of ozone depletion within a volcanic aerosol layer associated with the eruption of Mount Agung (March 1963) cannot be easily ascribed to this mechanism since background Cl_y levels at this time were less than 1 ppb. Michelangeli et al. [1991] argue that NaCl from volcanic ash injected into the stratosphere would react, enhancing ClO values, and lead to ozone depletion. Any additional source of Cl_y could tip the balance between the chlorine and odd-nitrogen species at lower levels of sulfate aerosols.

Stratospheric chlorine loading (i.e., Cl_y abundances in the lower-middle stratosphere where the bulk of the ozone loss is observed to date [see WMO, 1992]) was about 2.8 ppb in 1991, the year of the Mount Pinatubo eruption, and about 2.1 ppb in 1983, the time of El Chichon. Figure 2a includes, as a dotted line, a calculation for $\gamma_2 = 0.0012$ with $Cl_y = 2.1$ ppb. The chlorine levels are indeed critical; the 33% increase in Cl_y from 1983 to 1991 results in equivalent ozone destruction for sulfate aerosol areas that are lower by a factor of 2.5! Two effects amplify: the asymptotic loss rates increase with Cl_y, and, more importantly, the suppression of NO_x through reaction (2) is enhanced at lower surface areas. Additional tests, in the laboratory and atmosphere, of the efficiency of the reaction of $ClONO_2$ on sulfate aerosols are needed.

Ozone depletion is approximately linear with volcanic aerosol area, but highly nonlinear with regard to chlorine abundances and temperatures. It should therefore be extremely patchy, occurring in regions with sufficient Cl_y and large concentrations of sulfate aerosols. The initial properties of the plume (i.e., tropospheric air with entrained stratospheric air) would look similar to perturbed stratospheric air with low O_3

and low NO_x; however, the other properties of the freshly injected air would appear quite different (e.g., low ClO and Cl_y, low NO_y, high N_2O, adiabatic lapse rates, extremely high aerosol concentrations with volcanic ash). In order for significant O_3 loss to occur, the initial plume must be mixed on a molecular scale with air containing stratospheric concentrations of Cl_y and O_3.

Compared with El Chichon, Mount Pinatubo (2-3 times the amount of sulfur [*Bluth et al.*, 1992], in an atmosphere with 33% more ambient chlorine) is many times more likely to have created some regions in the stratosphere that crossed the threshold of catastrophic chlorine-driven ozone loss during the first year following the eruption. Pinatubo offers a unique opportunity, and we await the measurements [*Grant et al.*, 1992; also M. R. Schoeberl et al., Tropical ozone loss following the eruption of Mount Pinatubo, manuscript in preparation, 1992; J. Waters et al., MLS observations of tropical ozone following Mount Pinatubo, manuscript in preparation, 1992].

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M. J. Prather, Department of Geosciences, UC Irvine, CA 92717