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Large Volcanic Eruption Could Damage Ozone, 2 Researchers Report

Sulfuric acid spewed into the stratosphere may foster reactions.

By PHILIP SHABECOFF

A MAJOR volcanic eruption could significantly accelerate the destruction of the earth's protective ozone layer by industrial chemicals, two atmospheric scientists have reported.

Such large eruptions are rare, usually occurring not more than once or twice a century, but scientists who reviewed the new findings said they underscored the urgency of efforts to protect the ozone layer.

In a report last month in the *Journal of Geophysical Research*, David J. Hoffman and Susan Solomon said that the same sort of chemical reactions that have taken place on ice clouds over Antarctica can occur anywhere in the world on sulfuric acid droplets from a volcanic eruption. Over Antarctica, the reactions depleted the ozone layer by up to 50 percent in the spring of 1987.

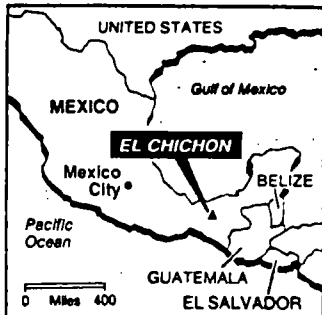
Dangers From Depletion

The depletion of atmospheric ozone, now widely attributed to emissions of chlorofluorocarbons and other industrial gases into the upper atmosphere, permits substantially higher levels of ultraviolet radiation from the sun to penetrate to the surface of the earth. Such radiation can increase skin cancer and cause eye cataracts and damage to the immune systems in humans, and it can harm plant, animal and marine life.

Dr. Hoffman, a physicist at the University of Wyoming, and Dr. Solomon, an atmospheric chemist with the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration, note that several scientific studies have suggested that the extinction of dinosaurs may have been linked to volcanic activity.

Evidence in recent years indicates that some volcanoes spew out chlorine compounds in addition to the large volumes of sulfuric acid produced in all eruptions. The chlorine compounds react with the sulfuric acid, thinning the ozone. Scientists theorize that the resulting increase in radiation killed the dinosaurs.

Although volcanic activity was much greater in that period than it is now, Dr. Solomon said in a telephone interview, the level of chlorine being



The New York Times/May 9, 1989

Stratospheric ozone fell sharply after 1982 eruption of El Chichón.

sent into the atmosphere by human activity is now far higher than the amount of chlorine that could come from natural sources.

A large volcanic eruption, such as one that destroyed the island of Krakatoa in 1883, could establish conditions for catastrophic additional depletion of stratospheric ozone, the paper suggests.

Such a large eruption, the paper says, "would provide an important test of this dinosaur extinction theory and perhaps determine whether contemporary biological systems may also go the way of the dinosaurs."

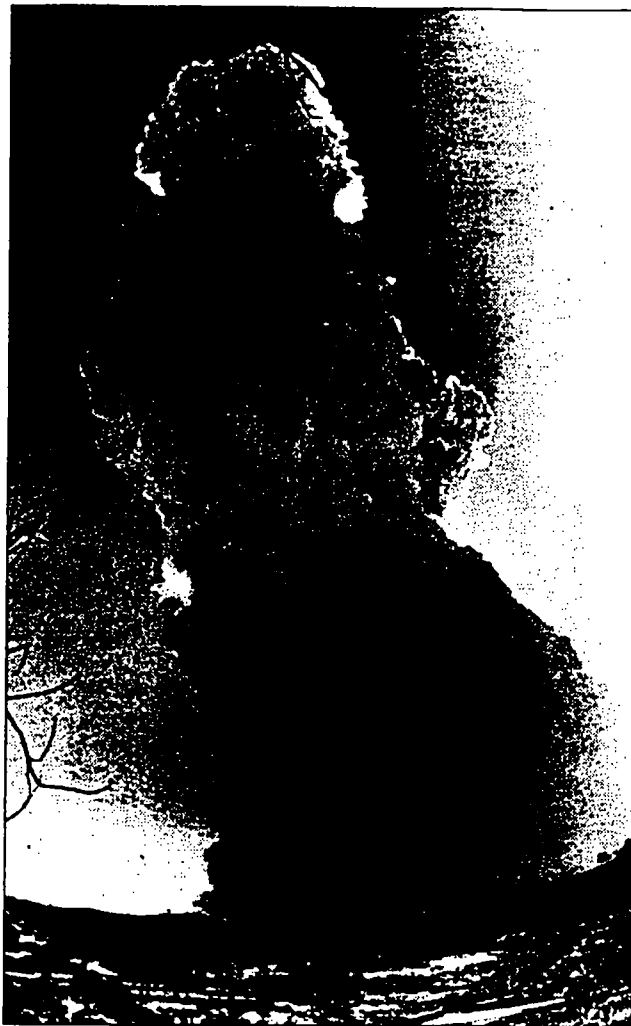
Dr. Solomon emphasized that the eruption would have to be powerful enough to propel the sulfuric acid into the stratosphere. Smaller eruptions, she said, tend to send gases no higher than the lower atmosphere.

A scientist who reviewed the paper, Dr. Ralph Cicerone, director of the atmospheric chemistry division of the National Center for Atmospheric Research, said the possibility that destruction of the ozone layer could be accelerated by volcanic activity is "a potential bombshell."

"What is startling about the paper is that while there have been volcanoes throughout history, now we have put chlorine in the air with chlorofluorocarbons and that means volcanic activity is at least partially capable of destroying the ozone layer," Dr. Cicerone said.

Dr. Hoffman and Dr. Solomon said that after the eruption of El Chichón in Mexico in 1982 there was a sharp reduction in stratospheric ozone in the mid-latitudes of both hemispheres, for which there appeared to be no explanation.

Since then, studies have found that ice formations on clouds in Antarctica provided a surface for chemical reactions in which freed chlorine



United Press International

Outpouring of steam and ash from El Chichón in Mexico. Previously unexplained ozone drop after the eruption has now been linked to chemical reactions on the surface of sulfuric acid droplets from the volcano.

radicals from chlorofluorocarbons react with and destroy ozone, a gas comprised of three oxygen molecules.

The two scientists developed computer models that suggested that sulfuric acid droplets from El Chichón could also provide a surface for chemical reactions with the industrial gases, although the reaction is somewhat slower and less intense than it is on the ice crystals.

The findings suggest that chemical reactions that can destroy the ozone layer can happen anywhere in the world if there is a large volcanic eruption, Dr. Solomon said. She said there are other sources of sulfuric acid in the upper atmosphere that provide a surface for the reaction of industrial chlorine, which is spread around the world, to destroy ozone.

Margaret A. Tolbert, a chemist at SRI International, a research organization in California, said the Hoffman-Solomon study shows that the kind of chemical reactions studied intensively over Antarctica can be found anywhere in the world.

Under an international agreement in 1987, production of chlorofluorocarbons is being limited to 1986 levels by most producing countries. The countries have also committed themselves to reduce production by 50 percent by the end of the century. But since the agreement was reached, evidence has shown that ozone depletion is more rapid than previously realized and many of the countries have called for a complete elimination of the chemicals.

So this Solomon would suggest that Solomon would guess that heterogeneous chemistry is at work in the mid-latitudes.

A volcanic eruption now could shred the polluted ozone layer

By Jeff Nesmith

A- Constitution Washington Bureau

WASHINGTON — Even if the world drastically curtails the use of ozone-destroying chemicals, a large volcano could touch off a catastrophic worldwide ozone

sometime in the next 20 or 30 years, scientists warned Wednesday.

A volcano similar in size to the 1982 El Chichon eruption in

Mexico would accelerate chemical reactions between ozone and millions of tons of chlorofluorocarbon chemicals that will continue to float in the atmosphere for years after use of the substances has ended, said Guy F. Brasseur, a physicist at the National Center for Atmospheric Research in Boulder, Colo.

In effect, conditions similar to those that cause annual ozone "holes" to appear over Antarc-

ca would develop over the entire planet, he said.

Within weeks, up to 12 percent of the protective gas would vanish from the stratosphere over populated areas of North America, Europe and Asia.

The calculations assume that 95 percent of the use of chlorofluorocarbons, known as CFCs, would be phased out by the year 2000, as called for under the Montreal Accord, a treaty to end

the use of the ozone-destroying chemicals.

Even with the phaseout, however, conditions have been primed for the complicated interactions among volcanic gas, ozone and chlorofluorocarbons that would remain in the atmosphere for years after emissions stop, Dr. Brasseur said. Therefore, no one can avert the ozone loss that would occur with a large volcanic eruption.

"There is nothing we can do," Dr. Brasseur said. "We can only hope that such a volcano does not occur."

Typically, an eruption the size of El Chichon occurs every few decades.

A loss of 12 percent of the ozone would be about twice as much depletion as scientists have recorded since the discovery that chlorine from CFCs was depleting ozone from the

stratosphere.

In the stratosphere, ozone protects the Earth's surface from ultraviolet radiation from the sun. Additional ultraviolet radiation would increase incidence of skin cancer and damage crops and fisheries, scientists say.

According to some calculations, a loss of 12 percent of the ozone would lead to increases of up to 48 percent in incidence of melanoma.

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in Good Old
Pope Romance*

Ozone Destruction Through Heterogeneous Chemistry Following the Eruption of El Chichón

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It is now well established that heterogeneous reactions provide an important mechanism for Antarctic ozone depletion. Recent laboratory studies suggest that the same reactions that occur on $\text{HNO}_3/\text{H}_2\text{O}$ ice clouds in the cold Antarctic stratosphere can also take place on sulfuric acid particles (e.g., volcanic and background aerosols) typical of lower latitudes, albeit at slower rates. The reduction in stratospheric ozone observed at northern mid-latitudes in late 1982 through 1983 following the volcanic eruption of El Chichón is investigated in terms of ozone loss through heterogeneous chemistry on the aerosol which formed in the stratosphere. The rates of the relevant heterogeneous reactions are believed to be critically dependent on (1) the aerosol surface area density and (2) the percent by weight sulfuric acid in the liquid particles. Direct measurements of both of these important quantities for El Chichón aerosol are described and used as a basis for model calculations of their possible effects on ozone and other trace species. The observed volcanic particle surface area reached a maximum at mid-latitudes of about $50 \mu\text{m}^2 \text{cm}^{-3}$ (above a typical background value of about 0.75) at an altitude of 18–20 km in early 1983. This enhancement of surface area is about the same as that encountered in stratospheric clouds in the Antarctic, suggesting a possible basis for ozone depletion through heterogeneous chemistry. Observations of NO_2 and HNO_3 also suggest that heterogeneous reactions on both background and volcanic aerosol play a significant role in partitioning reactive nitrogen species in middle and high latitudes in winter. It is shown that heterogeneous reactions similar to those occurring in Antarctica may have been responsible for at least a portion of the anomalous ozone reduction observed at mid-latitudes in early 1983.

1. INTRODUCTION

The observation of an anomalous reduction in ozone at northern mid-latitudes in late 1982 and most of 1983 appeared to be closely coincident with one of the largest volcanic perturbations of the stratosphere in the past century, that due to the eruption of El Chichón in Mexico in 1982. Total ozone fell to record lows at many observatories, more than 10% below normal in December 1982 and the first few months of 1983. Investigations as to whether a causal effect existed have been generally inconclusive. Hofmann and Rosen [1989] considered the possibility of a reduction of ozone following the eruption through purely kinetic loss to the aerosol and concluded that a reduction could have resulted at mid-latitudes if the probability of loss of ozone upon collision with the aerosol was greater than 10^{-6} . Only upper limits of this order exist in the available laboratory measurements, so that ozone loss through this direct mechanism is doubtful. Bojkov [1987] noted that an ozone reduction of the same magnitude (though of a different temporal and spatial nature) occurred in 1985 (when the El Chichón aerosol was substantially reduced) and concluded that most of the apparent ozone loss in 1983 and 1985 could be accounted for through unusual transport effects related to the quasi-biennial oscillation (QBO) and El Niño-Southern Oscillation (ENSO) but that possibly as much as one third of the total reduction in ozone in 1983 might be ascribable to the El Chichón eruption. Newell and Selkirk [1988] argued

that a substantial portion of the 1982–1983 ozone reduction may have been due to volcanic emissions, based on both an analysis of the temporal spread of the depletion and on statistical studies including QBO effects.

The discovery of the Antarctic ozone hole and subsequent theoretical studies involving heterogeneous chemistry on polar stratospheric cloud particles have changed the course of stratospheric ozone research [see Farman *et al.*, 1985; Solomon *et al.*, 1986; McElroy *et al.*, 1986a; Solomon, 1988, and references therein]. Laboratory studies have demonstrated that ice surfaces are surprisingly efficient in converting the inert chlorine reservoirs, ClONO_2 and HOCl , into more reactive compounds such as Cl_2 and HOCl , which readily release chlorine radicals through photolysis [Molina *et al.*, 1987; Tolbert *et al.*, 1987, 1988b; Leu, 1988a, b]. Of nearly equal importance to the Antarctic ozone depletion is a concomitant suppression of gas-phase reactive nitrogen radicals (especially NO_2), both through formation of the relatively long-lived species HNO_3 and through direct removal onto ice particles [Toon *et al.*, 1986; McElroy *et al.*, 1986b; Crutzen and Arnold, 1986]. Reduced NO_2 levels are critical to the efficiency of ozone destruction by heterogeneous reactions, since they determine the time scale during which the released chlorine remains available for reaction (rather than reforming the ClONO_2 reservoir).

The chemistry of the lower stratosphere is thus highly coupled, and Antarctic observations have revealed that the composition is greatly perturbed not only in terms of the ozone and reactive chlorine distributions, but also in terms of the abundances of NO_2 , H_2O , and other constituents [see Solomon, 1988, and references therein]. The surprising

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efficiency of heterogeneous reactions raises the question of the possible importance of stratospheric particles in general, especially following major volcanic eruptions which can greatly increase the available surface area. While these particles contain mostly sulfuric acid, in the colder regions of the stratosphere they can contain as much as 40% water by weight. Recent measurements by *Tolbert et al.* [1988a], *Worsnop et al.* [1988], and *Mozurkewich and Calvert* [1988] suggest that heterogeneous reactions similar to those occurring on Antarctic ice clouds can take place to some extent on liquid and solid sulfuric acid surfaces, provided that they contain a certain amount of water (see Figure 9). These facts suggest that a reevaluation of the observations following the eruption of El Chichón should be made, with inclusion of the new laboratory measurements. In this paper we discuss the ozone observations following the eruption of El Chichón, briefly review observations of other trace gases after the eruption which may be linked to possible variations in ozone chemistry, describe in situ aerosol observations following the eruption of El Chichón (investigating in particular those aerosol properties which are important for heterogeneous reactions), and estimate the ozone reduction that may have occurred as a result of heterogeneous chemical effects.

2. OZONE REDUCTIONS FOLLOWING THE ERUPTION OF EL CHICHÓN

At the Quadrennial Ozone Symposium held at Halkidiki, Greece on September 3–7, 1984, several papers were presented which suggested a possible reduction of ozone coincident with the presence of El Chichón aerosol cloud [*Bais et al.*, 1985; *DeLuise et al.*, 1985; *Deutsch*, 1985; *Komhyr et al.*, 1985]. Figure 1 [from *Bais et al.*, 1985], shows some of this evidence. Total ozone levels were considerably below normal at mid-latitude stations in the winter of 1982–1983, coincident with the maximum in the total aerosol mass at Laramie, Wyoming. An analysis of data from 18 northern hemisphere Dobson ozone spectrophotometer stations by *Mantis et al.* [1986] is shown in Figure 2. This analysis revealed that the total ozone decrease was the largest in the 20 years of data analyzed, that it occurred mainly from December 1982 through April 1983, and that it was largest at extratropical stations (an average reduction of about 30 Dobson units (DU) for 15 stations between the latitudes of 32°–59°N). During the same time period, subtropical stations (three between the latitudes of 10° and 25°N) indicated a smaller reduction (10–15 DU). Ozone measurements at Payerne, Switzerland [*Deutsch*, 1985], showed the deficit to be centered in the 20-km altitude region and to be in the 10–20% magnitude range.

The analysis by *Bojkov* [1987] mentioned earlier included total ozone and ozonesonde data from the northern mid-latitude observatories of Hohenpeissenberg and Payerne as well as Umkehr data from Arosa, with observations extended through 1985. These data show that the major differences between the 1983 and 1985 ozone decreases were the altitude intervals affected and the temporal variation of the deficit. The 1983 decrease was considerably more pronounced in the 16- to 19-km region of maximum aerosol surface area (see Figure 8) than that in 1985. Further, the 1983 ozone level gradually recovered throughout 1983. Finally, the 1983 reduction displayed relatively little ozone change at higher altitudes, whereas the 1985 event was characterized by a shorter-lived decrease which peaked at

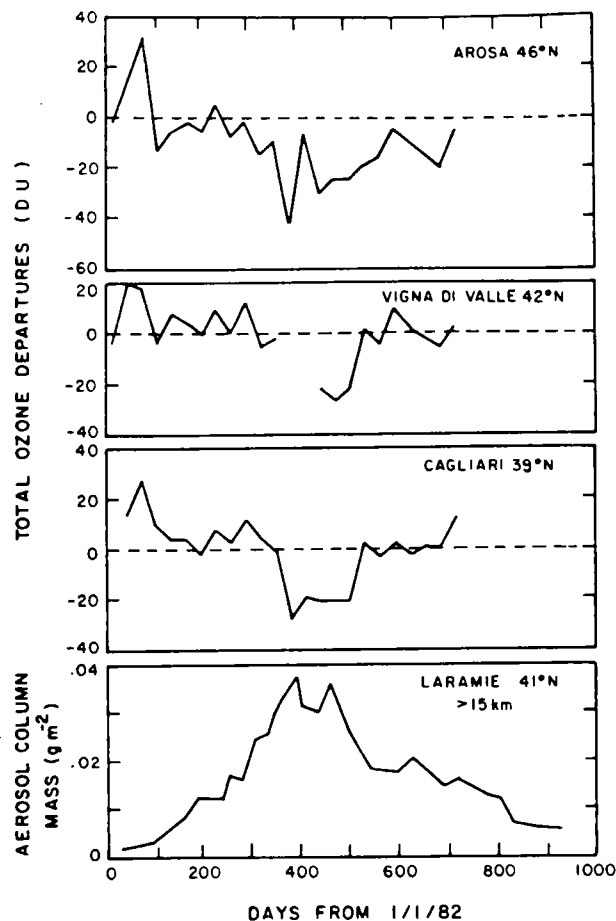


Fig. 1. Mid-latitude total ozone departures and stratospheric aerosol column mass as a function of time after the eruption of El Chichón [from *Bais et al.*, 1985].

28–30 km. The conclusion by *Bojkov* [1987] that both events were mainly caused by transport effects does not explain this pronounced difference in the altitude regime affected and the differing temporal variations. If one asserts that the high-altitude effects are transport related, since insufficient aerosol is present here to cause ozone reduction, then this component was less than half as strong in 1983 as in 1985. Thus a sizable portion of the 1982–1983 decrease at lower altitudes could be nontransport related and possibly due to the volcanic emissions.

Stolarski and Krueger [1988] analyzed TOMS measurements of total ozone in the northern hemisphere and reported reductions of the order of 10% in both 1983 and 1985. However, the 1983 reduction was rather uniform spatially, while the 1985 reductions were localized and were accompanied by increases of similar magnitude at some locations. This wavelike pattern suggests that the latter event was probably related to transport effects, while that in 1983 may have been associated with other processes.

H. Jaeger and J. Wege (personal communication, 1988), using the Hohenpeissenberg ozonesonde data and the nearby Garmisch lidar data for the period 1967–1987, found an ozone partial pressure reduction relative to the 20-year average of about 30 nbar at 18–21 km both in early 1983 and in 1985. The 1983 data closely followed the rise in late 1982 and decay throughout 1983 of volcanic aerosol, as indicated by the lidar, while the 1985 ozone reduction lasted only the first 4 months of the year and was not associated with a

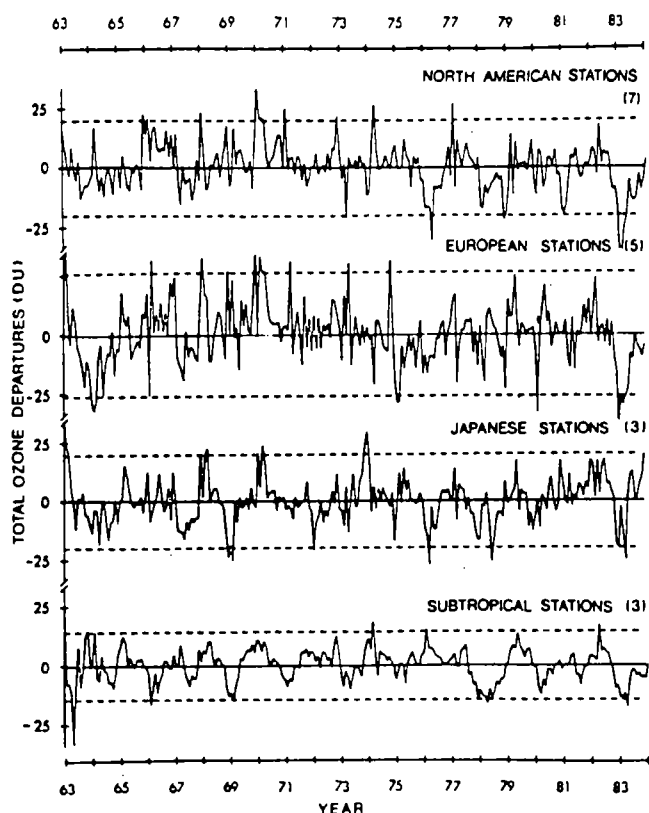


Fig. 2. Twenty-one years of total ozone measurements at 18 stations versus time [from Mantis *et al.*, 1985].

corresponding aerosol increase. At lower altitudes (15–18 km) a similar ozone reduction and aerosol increase were again well correlated in 1982–1983, but the 1985 data indicated little ozone reduction. At 21–24 km the data were similar to 18–21 km, except that the magnitude of the ozone reduction was reduced to 15–20 nbar. At 24–27 km there was little variation in either ozone or aerosol in 1982–1983, while 1985 indicated a continued ozone reduction of about 15 nbar, showing that the altitude variation of the ozone reduction was different for the two periods. Neglecting the periods near the volcanic eruptions of Fuego in 1974 and El Chichón in 1982, six QBO cycles could be identified in the 20-year data record and used to investigate the characteristics of the QBO effects on the ozone distribution. A mean QBO peak-to-peak ozone partial pressure variation of about 12 nbar was obtained at 18–21 km for Hohenpeissenberg. Subtracting the estimated QBO variation left a residual 10-nbar ozone reduction at 18–21 km in late 1982 to early 1983 and another of less than ~5 nbar in early 1985. This suggests the possibility of a volcanic effect of the order of 10% in this region in 1982–1983.

3. TRACE GAS MEASUREMENTS FOLLOWING THE ERUPTION OF EL CHICHÓN

The possibility that ozone could be altered through the direct injection of a number of trace gases must be considered. Most prominent in volcanic eruption effluents is SO_2 , which according to the contamination of the remote ozone-sensing instrument on the Nimbus 7 spacecraft [Krueger, 1983], was estimated to amount to at least 3.3 megatonnes (Mt) in the initial plume. The latter is believed to be a lower limit, as the initial cloud was optically thick (A. Krueger,

personal communication, 1988). H_2S would rapidly be converted to SO_2 in the eruption plume, so that the observed SO_2 is thought to represent a lower limit to the total amount of sulfur injected. Within a few months the injected SO_2 and H_2S should have entirely converted to H_2SO_4 vapor and condensed on aerosols [Hofmann and Rosen, 1984c]. Balloon-borne particle counter measurements and airborne lidar measurements suggest that at least 12 Mt of aerosol formed in the stratosphere [McCormick *et al.*, 1984; Hofmann, 1987]. This implies that at least 6 Mt of $\text{SO}_2/\text{H}_2\text{S}$ were in the initial plume (for a 75% H_2SO_4 , 25% H_2O aerosol composition). Detailed model calculations suggest that the possible effects of such injections are dependent on the consumption and generation of the OH radical during the oxidation of SO_2 and H_2S , but current best estimates indicate that ozone was not significantly depleted by sulfur chemistry following the El Chichón eruption [Crutzen and Schmaizl, 1983; McKeen *et al.*, 1984].

On the other hand, injected water vapor could increase the OH level and thus alter ozone chemistry. Although it is quite probable that some water vapor was injected into the stratosphere by the eruption, no in situ measurements of water vapor were made during the first year after the eruption at the initial extreme altitude of the eruption cloud (about 25 km). Ground-based measurements of the OH column at Boulder, Colorado, [Burnett and Burnett, 1984] indicated an increase of about 30% above the mean in mid-1982. This may be indirect evidence of an increase in water vapor and will be discussed further later.

Changes in odd nitrogen in the stratosphere could affect the ozone level. It is clear that dramatic decreases in Antarctic odd nitrogen are an essential element in the heterogeneous ozone loss there [McKenzie and Johnston, 1984; Mount *et al.*, 1987; D. W. Fahey, D. M. Murphy, C. W. Eubank, K. K. Kelly, M. H. Proffitt, G. V. Ferry, M. K. W. Ko, M. Loewenstein, and K. R. Chan, Measurements of nitric oxide and total reactive nitrogen in the Antarctic stratosphere: Observations and chemical implications, submitted to the *Journal of Geophysical Research*, 1988; hereafter referred to as Fahey *et al.*, submitted manuscript, 1988]. NO and NO_2 were observed to be about a factor of 2 below normal in the 30- to 35-km region at Palestine, Texas, in October 1982 [Roscoe *et al.*, 1986], and satellite observations suggest that enhanced aerosol levels extended to about 35 km immediately after the eruption [Thomas *et al.*, 1983]. No in situ observations of NO and NO_2 are available in the 20-km region where the bulk of the aerosol resided following the eruption. However, total column NO_2 measurements at Boulder, Colorado (40°N) showed a pronounced decrease (by about a factor of 2) coincident with the poleward movement of the El Chichón cloud in late 1982 (J. F. Noxon, personal communication, 1983). Smaller decreases were observed by Noxon at lower latitudes near 30°N. Johnston and McKenzie [1989] reported measurements of the total NO_2 column at 45°S over the period from December 1980 to August 1987. This continuous record represents the most complete climatology of stratospheric nitrogen species during this period. Their study revealed an NO_2 column decrease of about 15–20% that was apparently associated with El Chichón, and the largest decreases were obtained in winter. The larger NO_2 column decreases measured by Noxon probably result from the much greater volcanic cloud thicknesses reported for the northern hemisphere [e.g.,

Clancy, 1986]. These apparent reductions in column and in situ NO_2 and its latitude gradient are important points that will be discussed further later. We are not aware of any measurements of HNO_3 for the period in question.

Chloride is a common component of volcanic ash, so that increased levels of chlorine-bearing molecules may be expected in the stratosphere following major eruptions [Stolarski and Butler, 1979]. The HCl column was measured through airborne infrared spectroscopy 3–6 months after the El Chichón eruption [Mankin and Coffey, 1984]. An increase of 40% was observed for latitudes between 22° and 35°N , the region affected by the eruption at the time of the measurements. An estimated 0.04 Mt of HCl (9% of the global stratospheric HCl burden) was believed to have resulted owing to the eruption. Thus it appears that El Chichón caused a significant perturbation to chlorine levels in the stratosphere in 1982.

4. STRATOSPHERIC TEMPERATURE PERTURBATIONS FOLLOWING THE ERUPTION OF EL CHICHÓN

Enhanced levels of particles in the stratosphere will result in stratospheric heating, owing to the absorption of solar radiation (for absorbing particles) and longwave Earth radiation, and surface cooling from loss of solar radiation due to stratospheric scattering and absorption. Following the El Chichón eruption, a heating of $3^\circ\text{--}4^\circ\text{C}$ at about 23 km was observed in low latitudes [Labitzke et al., 1983]. Such heating would perturb the ozone photochemistry and could result in an ozone decrease; however, model predictions suggest that this reduction would be less than 2% [Vupputuri and Blanchet, 1984]. A similar heating was not observed in the northern mid-latitude stratosphere where the aerosol was diluted through transport in late 1982 and the most pronounced ozone decrease was observed. Thus it is believed that temperature perturbations were not significant in altering ozone after the El Chichón eruption.

5. AEROSOL OBSERVATIONS FOLLOWING THE ERUPTION OF EL CHICHÓN

5.1. Particle Size and Sulfuric Acid Content

The Mexican volcano El Chichón (17.3°N) underwent several major eruptions in late March to early April 1982, culminating on April 4 in what is believed to be the eruption which most affected the stratospheric aerosol distribution. A great deal of new information was obtained on the stratospheric effects of this eruption through numerous techniques, including both in situ and remote sensing. These observations have been reviewed [Hofmann, 1987], and all will not be discussed here. Since the important parameter in the study of possible effects of the aerosol on ozone is particle surface area, knowledge of the aerosol size distribution is crucial for this study. In addition, the amount of water in the aerosol is important for heterogeneous processes, so that the composition of the aerosol must be known. Such information is available from in situ balloon-borne measurements conducted following the eruption. These data have appeared in the literature [Hofmann and Rosen, 1983; 1984a, b, c] and will be summarized here.

Since 1971 the vertical distribution of aerosols has been measured in approximately monthly balloon soundings to about 30 km at Laramie, Wyoming. The original two-channel ($r \geq 0.15$ and $r \geq 0.25 \mu\text{m}$) optical particle counter was augmented with a condensation nuclei ($r \geq 0.01 \mu\text{m}$) counter

in 1973 and a large-particle ($r \geq 0.95$, $r \geq 1.2$, and $r \geq 1.8 \mu\text{m}$) counter in 1980. Descriptions of these instruments have appeared in the literature [Hofmann et al., 1975; Hofmann and Rosen, 1982]. The El Chichón eruption of 1982 was the largest detected since measurements began at Laramie and indicated stratospheric aerosol mixing ratios nearly 2 orders of magnitude above the background level of 1979.

Owing to the season and QBO phase at the time of the eruption, winds below about 20 km were westerly, while those above 20 km were easterly. This resulted in two distinct aerosol layers, which persisted until the winter wind reversal above 20 km in late 1982. Transport to the north from the eruption latitude was much more rapid in the lower altitudes, so that the gaseous $\text{SO}_2\text{--H}_2\text{SO}_4$ cloud below 20 km was more rapidly diluted than in the layer above 20 km, which remained confined in the $10^\circ\text{--}30^\circ\text{N}$ latitude band until late in 1982. This concentration of sulfuric acid vapor resulted in the upper layer aerosol growing to much larger sizes and was the primary reason that the El Chichón eruption displayed such large optical effects and perturbations on remote sensing instruments. As a result, lidar returns were unusually large from the upper layer, while the lower layer was barely discernable [McCormick et al., 1984]. Transport northward of the upper layer occurred in late 1982 and resulted in maximum aerosol concentrations at Laramie in December 1982 and January 1983.

In order to characterize the aerosol size distribution adequately, it is necessary to extend measurements from condensation nuclei sizes ($r \approx 0.01 \mu\text{m}$) to large ($r \approx \mu\text{m}$) sizes. Over this size range, concentrations vary over 10 orders of magnitude. Using three optical counters to cover the range, more than 40 balloon soundings at Laramie and several in southern Texas were conducted following the eruption of El Chichón. Figure 3 shows a sample of the data obtained from one of these soundings. The large increase in $r \geq 0.01 \mu\text{m}$ aerosol at an altitude of about 29 km was associated with annual stratospheric warming events [Hofmann and Rosen, 1989] and will not be discussed here.

From data such as those in Figure 3, one can construct size distributions at any desired altitude. This is done in Figure 4 for the 20-km level. Both the differential $n(r)$ and the integral $N(>r)$ are shown. The mathematical model which was used was a lognormal distribution between $r = 0.01$ and $r = 0.25 \mu\text{m}$. Above this size a cubic spline was used to fit the observations from 0.25 to $1.8 \mu\text{m}$. Details of this aerosol model and calculated comparisons with lidar and filter samples have been reported and gave generally very good agreement [Rosen and Hofmann, 1986]. This type of size distribution will be used later to calculate total aerosol area and mass.

The composition of the aerosol has been investigated using the evaporation technique to measure the boiling point as a function of atmospheric pressure [Rosen, 1971]. Figure 5 shows a typical profile of the normal El Chichón aerosol during balloon ascent and the profile which survives heating the intake tube of the particle counter to 130°C on parachute descent. As can be seen, only a few percent of the $r \geq 0.15 \mu\text{m}$ aerosol survive in the 15- to 25-km main layer. By varying the temperature during a controlled balloon descent, it was possible to obtain a vaporization curve (vaporization temperature versus ambient pressure) of the aerosol in southern Texas about 6.5 months after the eruption. These data indicated that the aerosol composition was consistent with a sulfuric acid–water mixture varying from about 60%

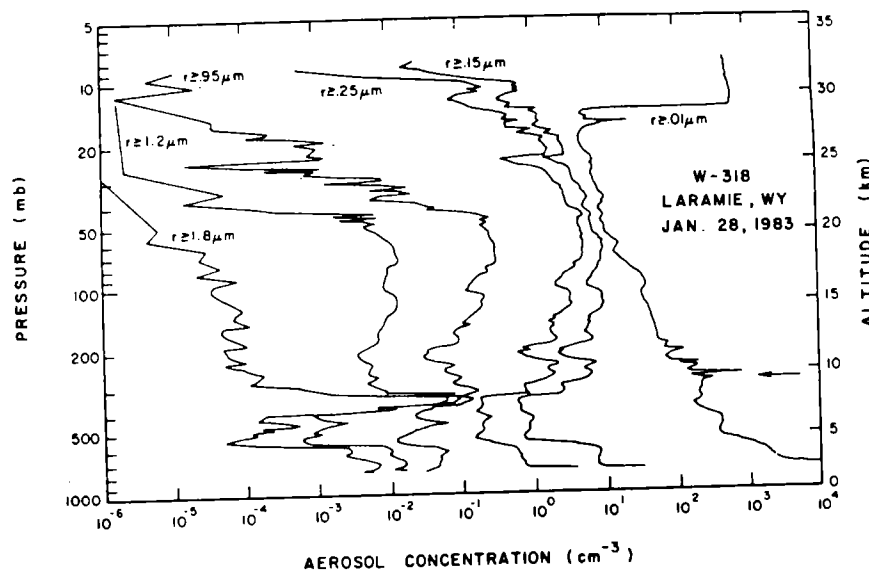


Fig. 3. Typical six-channel aerosol profiles at Laramie, Wyoming, following the eruption of El Chichón.

sulfuric acid in the colder regions near the tropopause to about 80% sulfuric acid in warmer regions at high altitude [Hofmann and Rosen, 1983, 1984b]. The measured sulfuric acid composition versus altitude is indicated in Table 1.

From the known size distribution and composition, the total aerosol mass mixing ratio could be determined. This parameter is shown along with the mass radius in Figure 6. The mass radius is the cube root of the average value of r^3 , averaged over the entire size distribution. The peak mass mixing ratio values of about 60 ppb are the largest ever measured in the stratosphere at Laramie. The measurements in southern Texas in 1982 indicated somewhat higher values initially. Figure 6 also shows the extent of the aerosol disturbance present before the eruption of El Chichón. The

latter was due to the eruption of Mount St. Helens in May 1980, Alaid in April 1981, and an eruption in Africa in January 1982. Although the decay of the mass mixing ratio does not appear to be uniformly exponential, an average decay time (e^{-1}) is about 1 year. Correcting for a background value of about 0.8 parts per billion by mass (ppbm) results in a decay time of about 10.5–11 months.

5.2. The Total Aerosol Surface Area After the Eruption of El Chichón

As indicated earlier, the total surface area of the aerosol distribution is an important parameter in heterogeneous reactions in the stratosphere. The characteristic time for deposition of molecules on the aerosol may be taken as the

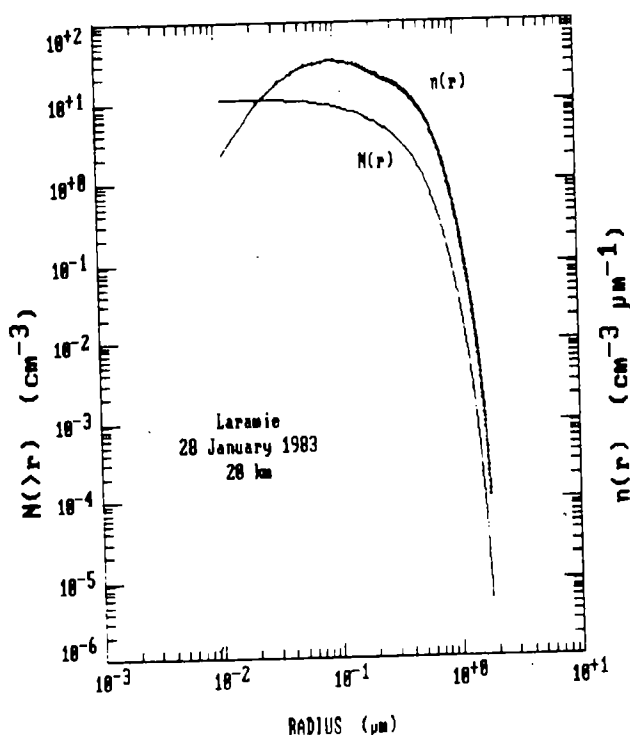


Fig. 4. Differential (n) and integral (N) aerosol size distributions determined from the data in Figure 3.

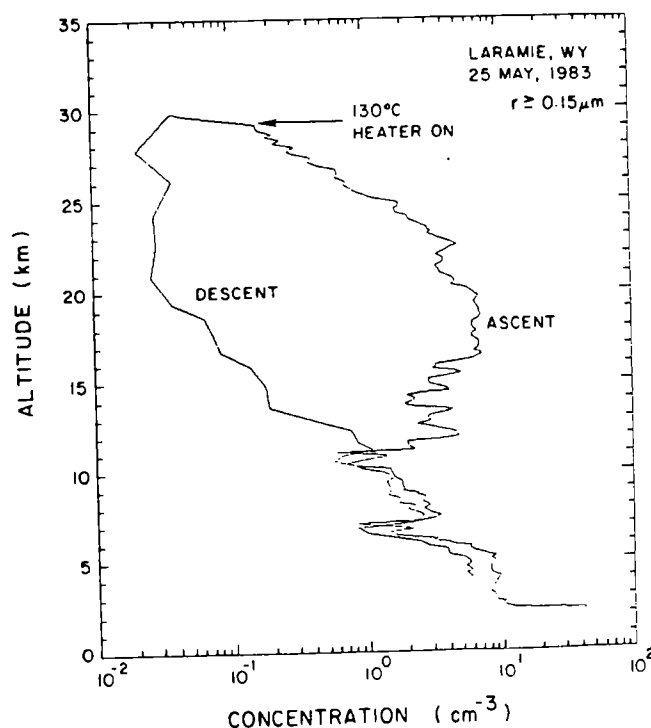


Fig. 5. Effect of heating the aerosol detector intake tube during parachute descent.

TABLE 1. Aerosol Composition, Sticking Coefficients, and Surface Area (28.5°N) October 23, 1982

Altitude, km	Temperature, °C	H ₂ SO ₄ , %		γ values ^b		Estimated Surface Area, $\mu\text{m}^2 \text{cm}^{-3}$	
		Measured	Theory ^a	ClONO ₂	HCl	Volcanic	Background
15.9	-65	61.0 $\pm$ 2.0	62.2	0.0060	0.0045	10	0.25
16.4	-65	62.7 $\pm$ 1.7	62.6	0.0040	0.0027	16	0.28
18.0	-65	60.5 $\pm$ 4.5	64.2	0.0065	0.0050	38	0.40
19.2	-65	60.5 $\pm$ 2.5	65.4	0.0065	0.0050	45	0.58
21.5	-58	73.5 $\pm$ 1.0	72.2	0.0004	0.00012	24	0.63
25.1	-53	79.5 $\pm$ 1.0	76.7	0.00011	0.000020	5.5	0.39
30.5	-47	78.8 $\pm$ 1.2	81.0	0.00013	0.000024	1.2	0.10

^aFor 5 ppmv H₂O, [Steele and Hamill, 1981].^bBased on measured H₂SO₄ weight %, [Hofmann and Rosen, 1984b].

e -folding time for removal of a molecular species through collision with the aerosol and is given by

$$\tau_a^{-1} = \frac{\gamma v A}{4}$$

where γ is the sticking coefficient, v is the molecular velocity (cm s^{-1}), and A is the aerosol surface area density ($\text{cm}^2 \text{cm}^{-3}$). The total surface area density of the aerosol size distribution is given by

$$A = \int 4\pi r^2 n(r) dr$$

where $n(r)$ is the differential aerosol size distribution at radius r . The area can be determined from the size distribution measurements, as discussed earlier. At times when the stratosphere is relatively free of volcanic aerosol (for instance, in 1979) the maximum total stratospheric aerosol surface area density is about $0.75 \mu\text{m}^2 \text{cm}^{-3}$. A few months after the El Chichón eruption a maximum surface area density of about $50 \mu\text{m}^2 \text{cm}^{-3}$ was observed in the dense aerosol layer between 20 and 25 km in southern Texas. At Laramie the area reached a maximum value of about $20 \mu\text{m}^2 \text{cm}^{-3}$ in early 1983. Figure 7 compares the mid-latitude aerosol area profile at the peak of the El Chichón event (January 1983) and at background in 1979. We see that it was about 25 times larger at 20 km in 1983 compared to 1979. Figure 8 shows the stratospheric peak aerosol area as a function of time after the eruption. Note that the high values in early 1983 are typical of the mid-latitude distribution at this time, while the high values observed in single soundings in late 1983 and early 1985 are not. The latter are associated with Arctic air, as can be ascertained by the low altitude of the peak area, also given in Figure 8.

It is interesting and perhaps surprising to note that the observed aerosol area range of $1\text{--}50 \mu\text{m}^2 \text{cm}^{-3}$ for El Chichón corresponds closely to the range of areas estimated for stratospheric clouds in Antarctica [Toon *et al.*, 1986], which are believed to be at the root of ozone depletion there. Since the latter clouds are believed to be either largely water ice or solids composed of nitric acid and water, the sticking coefficients for impinging gas molecules such as ClONO₂ are likely to be different than those for a sulfuric acid-water mixture. However, as already mentioned, substantial sticking coefficients for all of these classes of particles have recently been measured, suggesting that the presence of water on a surface may be an important factor linking these

very different surfaces. These considerations will be discussed in section 6.

6. HETEROGENEOUS CHEMISTRY

Until recently, laboratory data related to possible effects of particle distributions on stratospheric trace gases were few. Baldwin and Golden [1979] measured the reaction probability of many atmospheric species with a bulk concentrated sulfuric acid surface. Among the species investigated was ozone, which showed no detectable reactivity with sulfuric acid in their system. They estimated an upper limit of 1 reaction in 10^6 collisions. They also investigated whether the sulfuric acid would act as a catalyst for reactions

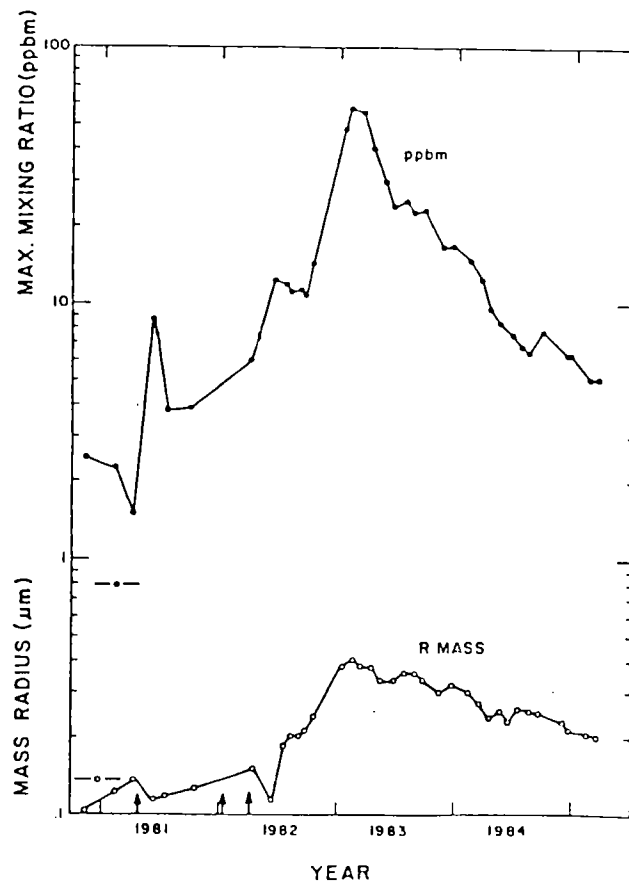


Fig. 6. Mass mixing ratio and effective mass radius versus time [from Rosen and Hofmann, 1986]. The individual points with horizontal lines to the left of the figure indicate background values. The arrows indicate major volcanic eruptions (see text).

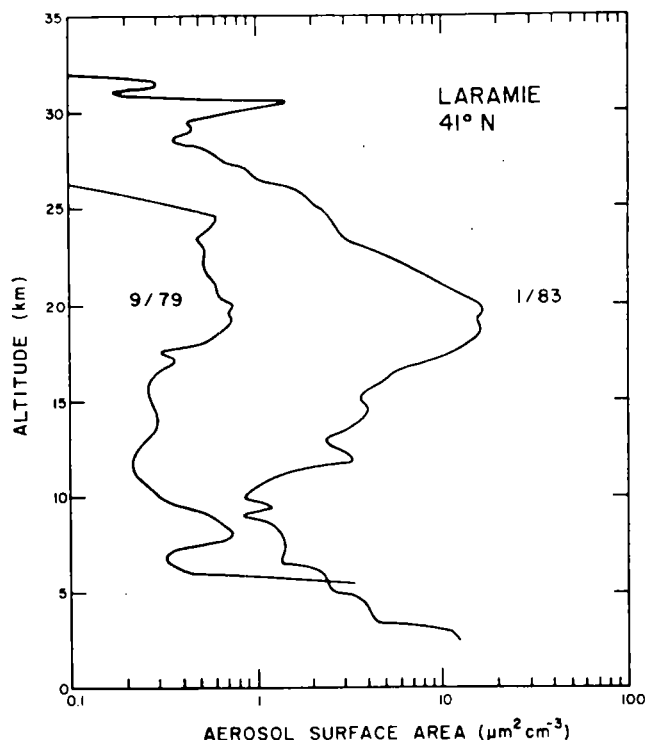
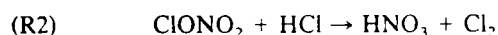
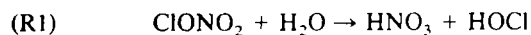


Fig. 7. Total aerosol surface area profiles at the peak of the El Chichón event and at background.

involving NO, NO₂, and SO₂. No reactions were observed at their sensitivity level. All of the experiments were conducted at 300 K and 270 K. No enhancements were observed at the lower temperature. They did not investigate reactions at stratospheric temperatures, nor did they consider mixtures of sulfuric acid and water.

Recent laboratory measurements of the reactions

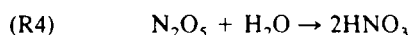
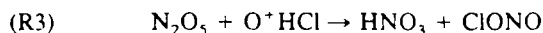


on 65–75% H₂SO₄ surfaces at 210–230 K [Tolbert *et al.*, 1988a] indicate surprisingly large sticking coefficients of about 2×10^{-3} for 65% H₂SO₄, 35% H₂O at 210 K, a composition consistent with that measured for the stratospheric aerosol in the 20- to 25-km region following the eruption of El Chichón, as shown in Table 1. Table 1 also displays calculated H₂SO₄ weight percent values for the flight at 28.5°N, based on thermodynamic data for H₂SO₄/H₂O mixtures, showing that the measured H₂SO₄ values are in excellent agreement with predictions. Tolbert *et al.* noted that HCl readily dissolved in (but did not react with) liquid H₂SO₄/H₂O surfaces and that the presence of a few hundredths of a percent of HCl in solution led to rapid rates for (R2) upon introduction of ClONO₂ into their laboratory system.

Figure 9 presents measured γ values for HCl and ClONO₂ on ice [Tolbert *et al.*, 1987; Molina *et al.*, 1987a; Leu, 1988a], and on sulfuric acid surfaces of varying composition [Tolbert *et al.*, 1988a]. Using the observations of Tolbert *et al.* on the variation of γ for HCl and ClONO₂ versus weight percent sulfuric acid over the limited range from 60 to 80%, as indicated by the lines in Figure 9, we have estimated the γ values appropriate for 28.5°N on October 23, 1982 (a date for which balloon aerosol measurements allow determination of the available surface area and percent sulfuric acid, as

shown in Table 1). The measured γ , aerosol surface, and H₂SO₄ content provide a basis for estimating the rates of (R1) and (R2). These numbers are given in Table 1.

Tolbert *et al.* [1988b] and Leu [1988b] also studied the behavior of N₂O₅ with HCl and H₂O on ice surfaces:



Large γ values of the order of 0.003–0.03 were determined in those studies.

The γ value for the reaction of N₂O₅ with water, (R4), on a 75% liquid sulfuric acid surface was recently determined to be 0.06 by Worsnop *et al.* [1988]. An entirely different technique was used by Mozurkewich and Calvert [1988] to study the same reaction on similar surfaces. The latter study was aimed primarily at the tropospheric effects of (R4) and was therefore carried out near room temperature. The reported sticking coefficient ranged from 0.05 to 0.09. The two studies taken together provide strong evidence for rapid heterogeneous reactions of N₂O₅ on sulfuric acid surfaces. The value of γ for (R3) has thus far been measured only on ice and not on sulfuric acid aerosol.

Although most of the laboratory studies described here have demonstrated that the indicated product molecules do indeed form in laboratory systems, most have not established quantitatively that the rate of appearance of product molecules equals the rate of disappearance of the reactants. The model calculations implicitly assume that this is so. The laboratory studies are often carried out on relatively large,

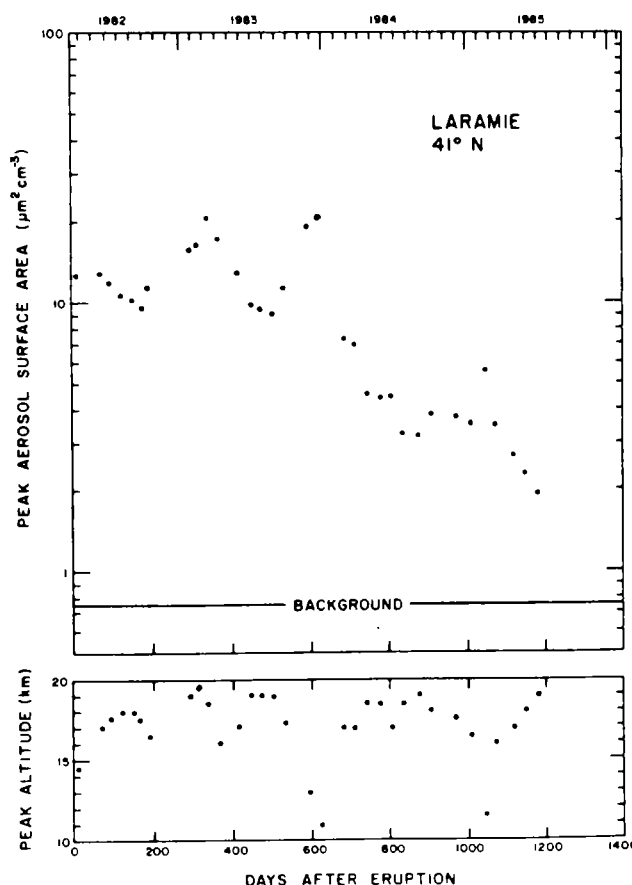


Fig. 8. Stratospheric peak total aerosol surface area and height of the peak versus time at Laramie after the eruption of El Chichón.

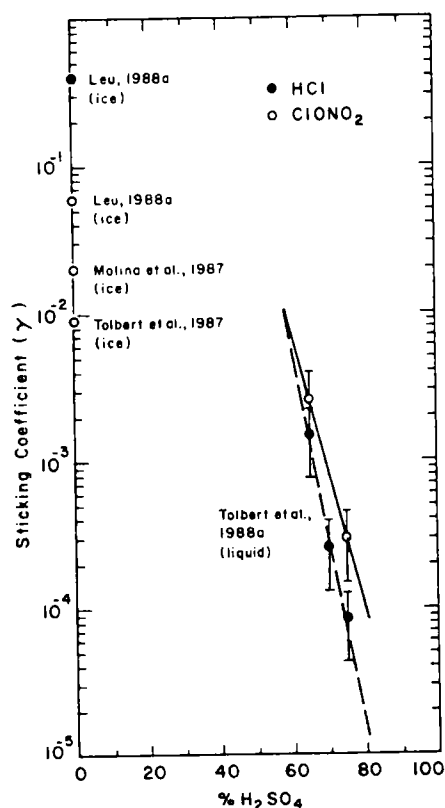
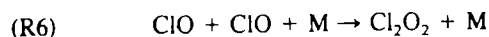
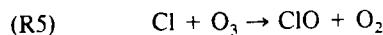


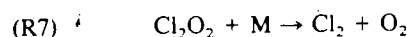
Fig. 9. Sticking coefficients for HCl and ClONO₂ on ice and on liquid sulfuric acid surfaces (for various weight percent solutions of H₂SO₄), as measured in laboratory studies.

flat surfaces, rather than on small, suspended particles. These considerations raise important questions regarding the application of laboratory studies in model calculations aimed at simulating these processes as they occur in the atmosphere. Nevertheless, the laboratory studies show that there is growing evidence for rapid surface reactions of HCl, ClONO₂, and N₂O₅ on sulfuric acid as well as on ice surfaces, raising the possibility that significant ozone depletion might take place on volcanic clouds as it does in Antarctica (see R. F. Turco, O. B. Toon, and P. Hamill (Heterogeneous physicochemistry of the polar ozone hole, submitted to the *Journal of Geophysical Research*, 1988) for a detailed study of the aerosol chemistry of reactions (R1) through (R4) in the Antarctic stratosphere). Further, the effect of these reactions on the normal background sulfuric acid aerosol layer might also provide smaller but significant contributions to the global stratospheric chemical balance [Rodriguez et al., 1988]. In order to understand the relationship between these rather different photochemical environments, we next summarize the probable role of (R1) through (R4) insofar as Antarctic ozone depletion is concerned.

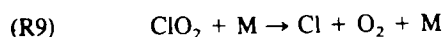
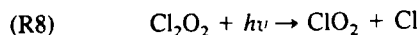
Reactions (R1) through (R3) convert the relatively inert HCl and ClONO₂ reservoir species into highly reactive forms of chlorine that release chlorine free radicals by photolysis. These go on to destroy ozone through the following reactions [Molina and Molina, 1987b]:



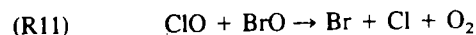
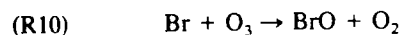
followed by



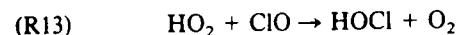
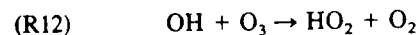
or



with much lesser contributions from reactions involving bromine [McElroy et al., 1986a]:



and hydrogen [Solomon et al., 1986; Crutzen and Arnold, 1986]:



The relative importance of each of these catalytic cycles in Antarctic spring is discussed by J. G. Anderson, W. H. Brune, S. A. Lloyd, W. L. Starr, M. Loewenstein, and J. R. Podolske, (Kinetics of O₃ destruction by ClO and BrO within the Antarctic vortex: An analysis based on in situ ER-2 data, submitted to the *Journal of Geophysical Research*, 1988; hereinafter referred to as Anderson et al., submitted manuscript, 1988) and R. L. Jones, et al. (Lagrangian photochemical modeling studies of the 1987 Antarctic spring vortex: Comparison with observations, submitted to the *Journal of Geophysical Research*, 1988).

In Antarctic spring these processes greatly perturb the local photochemistry, resulting in ClO abundances that are more than 100 times normal [de Zafra et al., 1987; Anderson et al., (submitted manuscript, 1988) and greatly reducing the abundances of NO₂ and NO_y [e.g., McKenzie and Johnston, 1984; Mount et al., 1987; Fahey et al., submitted manuscript, 1988], culminating in a massive depletion of atmospheric ozone that occurs on a time scale of the order of 3 weeks [Hofmann et al., 1987]. It is, however, critical to recognize that the direct condensation of HNO₃ also plays a substantial role in removing reactive nitrogen from the gas phase in the Antarctic spring lower stratosphere [Toon et al., 1986; McElroy et al., 1986b; Crutzen and Arnold, 1986]. This condensation takes place only at temperatures colder than about -80°C [Hanson and Mauersberger, 1988], and therefore will not occur in the warmer, mid-latitude stratosphere. This raises the question of the phase of the HNO₃ product of (R1) through (R4) at subpolar latitudes. At present it is not known if all of the HNO₃ produced in (R1) through (R4) returns to the gas phase or if some remains on the liquid aerosols. Measurements of the thermodynamics of the three-phase HNO₃-H₂SO₄-H₂O system would be required to evaluate this important matter quantitatively (although HNO₃ observations discussed later suggest that the HNO₃ likely remains largely in the gas phase). As mentioned earlier, measurements indicate that El Chichón may have injected a considerable amount of reactive chlorine into the stratosphere, perhaps directly enhancing the potential of halogen chemistry to deplete mid-latitude ozone [Stolarski and Butler, 1979] quite apart from consideration of possible heterogeneous processes. These uncertainties preclude a fully quantitative evaluation of the ozone depletion possible during El Chichón. It is, however, useful to examine some important time constants involved in stratospheric processes

TABLE 2. Parameters From Homogeneous Model Calculations for Estimation of Competition by Possible Heterogeneous Effects

Latitude	Pressure, mbar	Season	Non-CFC Chlorine, ppbv	τ_{HNO_3} Formation, s	τ_{Ozone} Loss	τ_{HCl} Loss
18	50	winter	0.29	1.1(6) ^a	8.5(7) ^b	4.9(6)
40	50	summer	0.65	1.0(6)	2.9(7)	3.1(6)
40	50	winter	0.75	2.3(6)	5.9(7) ^b	9.5(6)
18	10	winter	2.00	1.1(5)	1.1(6)	4.7(5)
40	10	summer	2.06	8.8(4)	6.3(5)	4.0(5)
40	10	winter	2.23	2.5(5)	1.4(6)	7.2(5)

^aRead 1.1(6) as 1.1×10^6 .^bThese photochemical loss times exceed the likely dynamical time scale.

and to consider the likely altitude and latitude distribution of the ozone depletion that could result from (R1) through (R4).

Reactions (R1) through (R4) will be of greatest potential importance to the ozone budget where the following conditions are met: (1) much of the total chlorine is in the form of HCl and ClONO₂ and thus available for conversion to chlorine radicals; (2) the time scale for photochemical replenishment of ozone is greatest; (3) the time scale for photolysis of HNO₃ is longest (if the HNO₃ remains in the gas phase); and (4) some sunlight is available. Table 2 presents representative estimates for these parameters at selected latitudes and altitudes, based on the two-dimensional model of Garcia and Solomon [1983] (see also later references to this model, as indicated by LeTexier *et al.* [1988]). Condition (1) is not met to best advantage in the tropical lower stratosphere, where the chlorine resides primarily in the form of chlorofluorocarbons that have not yet suffered conversion to reactive chlorine. Much greater abundances of free chlorine exist at higher latitudes as a result of atmospheric transport and photochemistry. Conditions 2 and 3 are most favorable in the lower part of the stratosphere at mid-latitudes in winter, compared to higher altitudes, lower latitudes, or other seasons. These trends are qualitatively consistent with observations mentioned earlier showing that the El Chichón ozone and NO₂ depletions were much larger in middle latitudes than in the tropics, in spite of greater aerosol loading there.

Let us consider the role of (R4) in perturbing the NO₂/HNO₃ ratio after the El Chichón eruption. The rate of production of HNO₃ by the gas-phase photochemical reaction between NO₂ and OH is about 1.8×10^3 molecule cm⁻³ s⁻¹ at 20 km, 39°N in winter. Assuming the aerosol properties given in Table 1 and a γ value of 0.06 as indicated by Worsnop *et al.* [1988], (R4) would result in an initial rate of HNO₃ production of about 1×10^5 molecule cm⁻³ s⁻¹, assuming the N₂O₅ concentration of the Garcia-Solomon model. As this greatly exceeds the normal gas-phase rate, it would clearly cause substantial changes in the HNO₃, N₂O₅, and NO₂ abundances, particularly in the middle- and high-latitude lower stratosphere in winter (see Table 2).

It is also interesting to consider the possible role of (R4) in affecting the distribution of NO_x species in nonvolcanically perturbed environments (i.e., on background sulfuric acid aerosol). A long-standing issue in photochemical modeling has been the inability of current photochemical/dynamical models to simulate the observed seasonal behavior of HNO₃ at high latitudes [Wofsy, 1978; Austin *et al.*, 1986; Jackman *et al.*, 1987]. Observations display maximum HNO₃ in winter and a minimum in summer, while models predict the

reverse. Austin *et al.* [1986] showed that (R4) could produce a HNO₃ source of sufficient magnitude to resolve the discrepancy if the γ characterizing this reaction were as little as 1.0×10^{-3} . Thus the measured values of 0.05–0.09 indicated by Worsnop *et al.* [1988] and Mozurkewich and Calvert [1988] are likely to have substantial effects on HNO₃ and NO_x abundances at sufficiently high latitudes in winter, where gas-phase photochemistry is slow, even when only the background sulfuric acid layer is considered (see Figure 10).

Tolbert *et al.* [1988a] suggest that the reaction of ClONO₂ with H₂O proceeds with an efficiency similar to that between ClONO₂ and HCl (i.e., comparable values of γ) on ice and sulfuric acid surfaces, although there is a substantial differ-

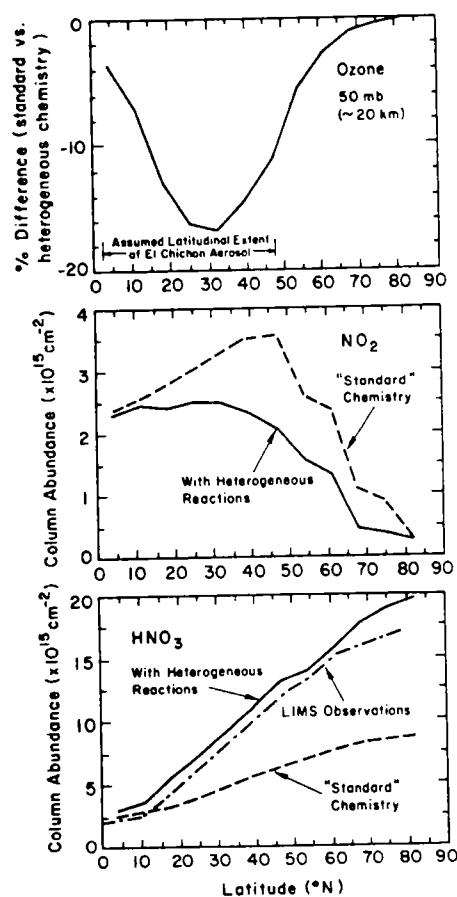


Fig. 10. Calculated changes (top) in ozone, (middle) in column NO₂ abundance, and (bottom) in column HNO₃ abundance due to El Chichón and background stratospheric aerosol, compared to gas-phase photochemistry only. HNO₃ column abundances measured by the LIMS experiment are also shown for comparison.

ence between the rates on the two types of surface. Since no measurements are available, we assume that the reaction between N_2O_5 and HCl on liquid sulfuric acid proceeds at the same γ value as that between N_2O_5 and H_2O , as measured by Worsnop *et al.* [1988]. Under these assumptions, (R3) can provide a potentially very efficient means of converting HCl to reactive chlorine on aerosol particles. Here it is appropriate to compare the rate of gas-phase destruction of HCl (through photolysis and reaction with OH) to the heterogeneous rate of (R3). At 39°N and 20 km these numbers would be about $100\text{ cm}^{-3}\text{ s}^{-1}$ and $5 \times 10^4\text{ cm}^{-3}\text{ s}^{-1}$, respectively, so that the heterogeneous loss may be as much as 500 times greater than homogeneous processes for the lower stratosphere at particular latitudes and seasons. The rates of (R3) and (R4) will change from these initial estimates as the processes in question alter the abundances of N_2O_5 and HCl and increase those of HNO_3 and ClO over time. However, these estimates demonstrate that (R3) has a strong potential to perturb reactive chlorine concentrations, as suggested by Tolbert *et al.* [1988b], while both (R3) and (R4) should be expected to have substantial effects on the abundances of NO_x and HNO_3 . Reactions (R1) and (R2) produce similar net effects. As the abundance of ClO grows and that of N_2O_5 declines as a result of decreasing abundances of NO_x , (R1) and (R2) will assume greater importance. The changes in ClO and NO_x species will also be accompanied by changes in the distributions of other chemical constituents, such as OH and HO_2 , and these may also influence the ozone budget. In particular, greatly reduced NO_x abundances significantly enhance the abundances of OH and HO_2 , and these in turn react directly with ozone in the lower stratosphere in an efficient ozone destruction chain.

We conducted a model calculation to estimate the possible role of such reactions, both for background sulfuric acid and for the El Chichón cloud. A detailed calculation of the growth, transport, and decay of sulfuric acid aerosol following a volcanic eruption requires aerosol model calculations, as shown by McKeen *et al.* [1984] and Capone *et al.* [1983]. Adriani *et al.* [1987] and D. V. Michelangeli, M. Allen, and Y. L. Yung (Impact of the El Chichón volcanic aerosols on stratospheric chemistry, submitted to the *Journal of Geophysical Research*, 1988) have also shown that volcanic aerosol can significantly affect the stratospheric radiation field. In the present study, aerosol surface areas are prescribed rather than calculated interactively, and the effects of aerosols on the radiation field are neglected.

Detailed methane oxidation chemistry, as described by LeTexier *et al.* [1988], was included in all model runs. The chemistry of Cl_2O_2 was included, and it was assumed that 50% of the thermal decomposition of Cl_2O_2 results in ozone loss, as suggested by Molina and Molina [1987], but bromine reactions were neglected. Table 1 shows the sensitivity of the heterogeneous reactions to variations in the weight percent of H_2SO_4 , at least for (R1) and (R2). Such information is not available for (R3) and (R4). We chose to use the γ values measured by Tolbert *et al.* [1988a] for (R1) and (R2), using our estimate of the appropriate values for 28.5°N , as shown in Table 1, for the altitude range from the lower boundary of the model at 16 km up to 30 km. These γ values were imposed at all latitudes without detailed consideration of the local temperature. To account crudely for the possible dependence of (R2) and (R3) on the gas-phase HCl mixing

ratio, we allowed these reactions to decrease linearly in their efficiency for gas-phase HCl mixing ratios less than 0.1 ppbv. For (R4) the measured γ value of Worsnop *et al.* [1988] for 75% sulfuric acid surfaces was assumed at all levels, and the same value was adopted for (R3), as discussed earlier. It was assumed that the product HNO_3 remained in the gas phase (see following discussion).

Within the latitude range from 4° to 47°N , the volcanically perturbed aerosol surface area was estimated based on the maximum measured values described earlier and indicated in Table 1. Background stratospheric aerosol densities, as shown in Table 1, were imposed at all other latitudes. The calculations were begun for the month of April and terminated at the end of January, although it is likely that the cloud did not spread to mid-latitudes until about October. We further note that observed surface areas at Laramie (Figure 7) in January were about a factor of 2 smaller than these adopted values, which are typical of the lower-latitude measurements closer to the center of the cloud. While there is clearly a great deal of uncertainty in all of these quantities, the prescribed scenario is reasonable and provides some potentially useful information for future attempts to detect the likely effects of such eruptions. The calculations were compared to a control run in which no aerosol reactions were included at all.

Figure 10 shows calculated changes in the NO_2 and HNO_3 column abundances, as well as the ozone mixing ratio at the 50-mbar level (roughly 20 km). Significant decreases were obtained in NO_2 and N_2O_5 , with corresponding increases in HNO_3 . HNO_3 column abundances measured by the Limb Infrared Monitor of the Stratosphere (LIMS) satellite experiment above 100 mbar in January 1979 are similar to other measurements of the HNO_3 column and can be directly compared to the model results [see Austin *et al.*, 1986, and references therein]. Figure 10 shows that the calculated HNO_3 total column abundances are in much better agreement with observations than those predicted without heterogeneous reactions. The calculated peak mixing ratio of HNO_3 increased from about 5 to 13 parts per billion by volume (ppbv) in the polar night region, which provides much better agreement with satellite measurements of about 10.5–12 ppbv [see Austin *et al.*, 1986], and supports the notion that much of the product HNO_3 probably remains in the gas phase. The calculated decreases in NO_2 were pronounced, especially at mid-latitudes, in qualitative agreement with the measurements by J. F. Noxon (private communication, 1983), Roscoe *et al.* [1986], and Johnston and McKenzie [1989].

The seasonal and latitudinal variations in the calculated NO_2 decreases depend on both the HNO_3 photolysis time scale and on the altitude and latitude distribution of NO_x (which is qualitatively similar to that of ClO_x for similar reasons; see Table 2 for representative values). Thus the largest NO_2 decreases are expected at middle and high latitudes in winter. Note that the calculated changes in NO_2 and HNO_3 are not confined to the latitudes where the El Chichón cloud is imposed, but extend to higher latitudes where only background sulfuric acid aerosols were considered. Model tests confirm that the high-latitude winter enhancements in HNO_3 are the result of local chemistry on background aerosols rather than mixing, consistent with the good agreement obtained relative to the LIMS measurements in January 1979, when stratospheric aerosol levels

appeared to be close to background values (Figure 7). These results suggest that (R1) through (R4) occurring on background as well as volcanic aerosols can decrease the abundances of NO, NO₂, and N₂O₅, while increasing those of HNO₃ and ClO, as compared to calculations neglecting heterogeneous reactions, especially near the polar night terminator in the lower stratosphere.

The local change in ozone at 50 mbar was greatest in winter at middle latitudes, as indicated earlier based on time scale arguments. The changes obtained in the tropics and in the summer were only a few percent, as expected from Table 2. A test case was also conducted using the smaller measured surface areas from the Laramie winter sounding (Figure 7), rather than the lower-latitude maximum values shown in Table 1. In this case a maximum local ozone depletion of 12% at 50 mbar 40°N was obtained.

It is important to note that the quantitative effects of eruptions of varying strength can be quite different from the numbers presented here, as a result of nonlinearities in chemical effects. Thus the estimates presented here should be interpreted as appropriate only to large eruptions and are highly dependent on the adopted γ values. They should therefore be interpreted as illustrative of possible effects rather than being definitive.

7. SUMMARY AND DISCUSSION

Evidence for changes in ozone and other stratospheric species due to the eruption of the El Chichón volcano has been briefly summarized. Measurements of aerosol surface area and weight percent H₂SO₄ in the volcanically perturbed region have also been discussed, with a particular view toward their implications for heterogeneous chemistry.

Recent laboratory studies have confirmed the rapidity of reactions involving HCl, ClONO₂, N₂O₅, and H₂O on ice surfaces, and growing evidence demonstrates the importance of such processes to the depletion of Antarctic ozone. Laboratory studies also suggest that these reactions can take place on sulfuric acid aerosols. These studies imply that NO_x species may be converted efficiently to HNO₃ and that reactive chlorine may be enhanced in volcanically perturbed regions, with attendant effects on atmospheric ozone.

It is also important to consider the possible effects of such reactions on background sulfuric acid aerosol. We have shown that the observed background sulfuric acid surface area, taken together with the sticking coefficients derived from laboratory studies, can have important effects on HNO₃ and NO₂ levels, particularly in high latitudes in winter. This reconciles a long-standing problem in photochemical modeling and has important implications not only for HNO₃, but also for measurements of other species such as NO, ClO, and ClONO₂, especially near the polar night terminator.

In summary, there are several important observations that agree well with the calculations indicated here. These are (1) observations showing the largest local ozone changes in the winter at mid-latitudes after the El Chichón eruption, in spite of greater aerosol loading in the tropics; (2) observations showing substantial ($\approx 50\%$) decreases in NO₂ abundances following El Chichón, particularly at middle latitudes in winter; and (3) observations suggesting an important source of HNO₃ in the middle- and high-latitude stratosphere under background conditions. On the other hand, a major discrepancy between these calculations and observations is the fact

that we estimate an HCl decrease of about 30%, while Mankin and Coffey [1984] observed a substantial increase of about 40%. The model calculations also do not yield significant changes in the total OH column abundance, in contrast with the observations of Burnett and Burnett [1984]. These observations suggest that the direct injection of chlorine and H₂O by the volcano may have been significant factors in determining stratospheric composition and hence in the observed ozone depletion.

Rodriguez et al. [1988] considered the possible influence of (R1) and (R2) occurring on background aerosol on global ozone depletion estimates. In one test case, Rodriguez et al. evaluated the impact of those reactions, assuming that they took place on background aerosol at about 1/200 their absolute rate on Antarctic polar stratospheric clouds. The measured background aerosol surface areas and sticking coefficients shown in Table 1 correspond to an efficiency for background aerosol which is about 1/1000 of that of Antarctic ice clouds for (R1) and (R2), but that for (R3) and (R4) may be closer to 1/100, assuming the sticking coefficients reported by Worsnop et al. [1988] and Mozurkewich and Calvert [1988] for (R4). Assuming an efficiency of 1/200 for (R1) and (R2), Rodriguez et al. [1988] estimated a global ozone decrease of slightly less than 1% for 1990 and about 5% for 2060. Reactions (R3) and (R4) should produce similar effects. These values should be compared to their calculations neglecting surface reactions, which yielded ozone changes of nearly zero for 1990 and less than 2% for 2060. Thus the study by Rodriguez et al., together with recent laboratory studies, shows that heterogeneous reactions may be an important factor to consider in estimates of the present and future global ozone response to increasing chlorofluorocarbon abundances, even when only the background sulfuric acid aerosol layer is considered. Decadal trends in the background sulfuric acid aerosol layer due to unusually high volcanic activity may be important, as well as seasonal and latitudinal variations in the potential for ozone depletion. The discussion presented in this paper illustrates that these reactions will be of greatest potential importance in middle to high latitudes in winter, where the reported current total ozone trends are largest [Harris et al., 1988].

Although chlorofluorocarbon emissions are likely to be reduced worldwide, it is also true that the chlorine in the current stratosphere will remain there for about a century. While the El Chichón volcano injected a substantial amount of material into the stratosphere, larger volcanic injections have certainly occurred over longer time scales (e.g., Krakatoa, Tambora). Indeed, it has been suggested that the extinction of the dinosaurs might have been related to a massive volcanic eruption [e.g., Officer et al., 1987, and references therein]. In the preanthropogenic atmosphere, such an effect could have taken place through the mechanism described here only if both aerosol and stratospheric chlorine were greatly enhanced by such an eruption. Under these circumstances, large-scale ozone depletion could have occurred, resulting in greatly enhanced ultraviolet penetration and attendant biological effects. In the present atmosphere the chlorine abundances have been greatly enhanced by anthropogenic emissions of chlorofluorocarbon, and further increases are anticipated in the next few decades even if control measures begin in the 1990's. A larger eruption than El Chichón occurring in the next half-century or so would therefore provide an important test of this

dinosaur extinction theory and perhaps determine whether contemporary biological systems may also go the way of the dinosaurs.

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Future changes in stratospheric ozone and the role of heterogeneous chemistry

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HETEROGENEOUS chemical reactions on the surfaces of solid or liquid particles present in the lower stratosphere may be an important influence on the levels of ozone depletion resulting from increased concentrations of anthropogenic chlorine compounds in the atmosphere¹. Such processes, occurring on ice particles in polar stratospheric clouds, have been invoked to explain the formation of the springtime ozone hole over Antarctica^{2,3}. Sulphuric acid aerosols injected into the atmosphere following a volcanic eruption may also provide sites for heterogeneous chemistry leading to ozone depletion⁴. Here we present model calculations that assess the importance of heterogeneous processes in future ozone depletion, assuming that trace-gas concentrations follow the protocol agreed at the recent international convention in London. We find that, even if this protocol is adhered to, reactions on the surface of sulphuric acid aerosol particles could produce significant ozone depletion into the beginning of the next century, especially if a major volcanic eruption (similar to the El Chichón eruption of 1982⁵) takes place.

Stratospheric aerosols (solutions of sulphuric acid in water) are present in the lower stratosphere at all latitudes. The aerosol layer, discovered by Junge⁶, extends from about 10 to 30 km altitude; the aerosol concentration, and therefore the area available for heterogeneous chemistry, is dramatically increased after large volcanic eruptions (such as El Chichón). Laboratory work has shown that sulphuric acid aerosols can convert nitrogen oxides such as N₂O₅ into nitric acid (HNO₃), and inactive chlorine reservoirs (ClONO₂, HCl) into reactive (ozone-depleting) chlorine (Cl, ClO)^{6,7}. As the rates of these processes, as well as their dependence on aerosol composition and temperature are still uncertain, we have used a range of plausible rates and have performed sensitivity studies.

For the sake of clarity, we consider here only one scenario for future increase in trace-gas concentrations. This scenario, summarized in Table 1, accounts for a 95% phase-out of CFC's by the year 2000 (London agreement, 1990). The level of chlorine (1 part per 10⁹ by volume (p.p.b.v.) in 1960 and 2.5 p.p.b.v. in 1980) will reach 4.5 p.p.b.v. in year 2010.

Figure 1a-c shows the calculated changes in the ozone column between 1960 and 2010 as a function of latitude and time of the year. The model⁸ used for these calculations is two-dimensional (latitude and altitude) and treats chemistry, radiative transfer and dynamics consistently in the stratosphere and mesosphere.

When heterogeneous processes are ignored (Fig. 1a), the calculated ozone depletions are modest: the reductions between 1960 and 2010 are typically 1% at the Equator; they vary with latitude, reaching 1% at 85°N and 1.5% at 85°S in late winter and early spring. The high-latitude ozone decrease is caused by downward transport of ozone-depleted air from the upper stratosphere during winter at high latitudes^{9,10}. Thus, when heterogeneous chemistry is neglected, the ozone depletion in the polar regions is primarily affected by the seasonal variation in the mean meridional circulation of the atmosphere. The positive changes seen at mid-latitude are caused by a cooling of the stratosphere resulting from the CO₂ increase (and consequently a reduced ozone destruction rate) and an enhanced

ozone production in the troposphere associated with the CH₄ increase. The global ozone reduction in this case is 0.22%.

When we included the effects of heterogeneous reactions on the surface of particles^{11,12} contained in polar stratospheric clouds (PSCs), the model showed dramatic ozone reductions in the polar lower stratosphere during the spring period and predicts a global ozone reduction of 3.6% between 1960 and 2010. Between 5 August and 5 October, the ozone density calculated at 85°S is reduced by 3% at 28 km, 68% at 25 km, 71% at 20 km, 59% at 15 km and 10% at 10 km. The October mean ozone column at the same latitude is reduced from 315 dobson units in 1960 to 295 in 1970, 245 in 1980, and 185 in 1990.

Finally, when we included the effects of stratospheric aerosols, the model predicted further ozone depletion. The composition

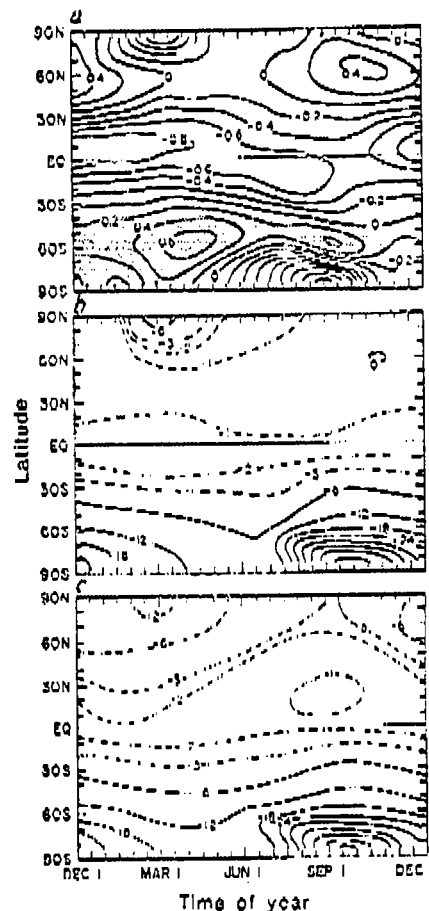


FIG. 1 Ozone column changes (per cent) as a function of latitude and season calculated between 1960 and 2010 when **a**, only homogeneous chemistry processes are taken into account; **b**, heterogeneous processes occurring on the PSCs in the polar regions are introduced; **c**, heterogeneous processes on both PSCs and sulphate aerosols are considered (reaction probabilities $\gamma_1 = 2.6 \times 10^{-3}$ and $\gamma_2 = 0.14$). The two-dimensional model used here extends from pole to pole and from the surface to 85 km altitude. The chemical scheme includes 56 species belonging to the O_x, HO_x, ClO_x, BrO_x, and SO_x families as well as methane and its oxidation products. Chemistry, radiative transfer and dynamics are treated interactively, above 10 km altitude, so that the most important feedbacks (such as ozone-temperature) are taken into account. When we included the chemical effects of the PSCs, we assumed that as the temperature of the lower stratosphere decreases below 199 K in the two polar regions, the two chlorine reservoirs HCl and ClONO₂ are converted with a time constant of 15 days into a more reactive form of chlorine (ClO, $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$) and that N₂O₅ is converted into HNO₃. When type II PSCs are formed below ~194 K, we assumed that the lower stratosphere is denitrified by gravitational sedimentation of the relatively large ice particles involved. The parameterization of the heterogeneous chemical processes on the surface of sulphate aerosol particles is described in the text. For each simulated case, the model was run to steady-state conditions with fixed boundary conditions.

TABLE 1. Concentrations used in the model simulations.

We have assumed a 95% phase-out of CFCs by the year 2000, with 50% of this reduction (in mass) being added to the base emission of HCFC-22 (which acts as a surrogate for all CFC replacement products, except the halons). CCl₄ was assumed to grow by 1 p.p.t.v. per year from 1960 to 1985 and 4 p.p.t.v. per year afterwards. CFC-11, CFC1₃; CFC-12, CF₂Cl₂; CFC-113, C₂F₃Cl₃; CFC-114, C₂F₄Cl₂; CFC-115, C₂F₅Cl; HCFC-22, CHF₂Cl; halon-1211, CF₃ClBr; halon-1301, CF₃Br.

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the values are uncertain by at least an order of magnitude. For the probability of reaction (1), γ_1 , Tolbert *et al.*⁶ report values of 3×10^{-4} and 2.6×10^{-3} for 75 and 65 wt% of acid, respectively. According to laboratory work using non-dispersive sulphuric acid aerosol¹⁶, the probability of reaction (2), γ_2 , could be as high as 0.09 (293 K) to 0.14 (274 K) and relatively independent of the relative humidity (1–10%). The value of γ_2 is not known for the solid or the supercooled sulphuric acid aerosols which would exist at stratospheric temperatures.

Figure 1c shows the change in the ozone column between 1960 and 2010 with the added influence of the background aerosol layer. For this calculation we used $\gamma_1 = 2.6 \times 10^{-3}$ and $\gamma_2 = 0.14$ (ref. 17). When comparing Fig. 1c to Fig. 1b, the addition of the background aerosol modifies the predicted ozone depletion, which is now 5.7%. For potentially larger values of the reaction probabilities, however, the contribution of aerosol particles becomes more significant; as shown by Fig. 2, the effect of aerosols at their background level on the global ozone budget becomes noticeable (additional ozone depletion of $\approx 1\%$) for γ_1 and γ_2 becoming larger than $\sim 3 \times 10^{-3}$ and 0.1, respectively.

For an aerosol load corresponding to a post-volcanic situation, the sensitivity of ozone to chlorine is substantially enhanced. Figure 3a, b shows the change in the ozone column resulting from an increase in aerosol surface area from the background to the post-volcanic situation, for unchanged concentrations of trace gases at their level of 1982 and 2010, respectively (see Table 1). The values of γ_1 and γ_2 are the same as those used for the model simulation shown in Fig. 1c. Figure 3b suggests that even with reduced emissions (nearly total phase-out) of CFCs in the future, a large volcanic eruption in year 2010 or so, could deplete ozone significantly at all latitudes: the depletion in global ozone calculated for 2010 is 2.3% larger than for the background aerosol case (total ozone depletion compared to 1960 including PSC and volcanic effects is 8%). The magnitude of the ozone change depends dramatically on the reaction probabilities used and laboratory investigations of these values as a function of temperature and aerosol composition are urgently needed. This last model calculation shows, however, that heterogeneous chemistry should affect the predictions of ozone change, especially if large quantities of aerosol particles are injected into the lower stratosphere (provided that the laboratory values derived for γ_1 and γ_2 are representative of sulphuric acid aerosols at stratospheric temperatures). Ozone depletion has been observed after the eruption of El Chichón^{4,18–20}. Since 1982, the level of chlorine in the atmosphere has increased by $\sim 30\%$ and it is expected to increase further by 2010. According to the model, the ozone sensitivity to volcanic eruptions should be twice as large in 2010 as it was in the early 1980s. Thus, despite limitations in the emissions of CFCs, noticeable changes of anthropogenic origin could be observed in the next 20 years. □

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Mechanism of the γ - β phase transformation of Mg_2SiO_4 at high temperature and pressure

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THE transformation of $\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$ olivine first to the β -phase (modified spinel) and then to the γ -spinel phase occurs with increasing depth in the Earth's mantle as a result of the increasing pressure^{1,2}. The mechanisms of these two transformations have an important influence on mantle rheology and may also be related to the origin of deep-focus earthquakes^{3–5}. We report here the results of experiments on the phase transformation of Mg_2SiO_4 olivine at 15 GPa pressure in a multi-anvil cell. At this pressure and a temperature of 900 °C, early formed metastable γ -spinel transforms partially to the β -phase. The observed microstructures, which are similar to those in shocked meteorites^{6–11}, show that the γ -to- β transformation can occur either by diffusion-controlled growth or by a martensitic (shearing) mechanism, depending on how far the pressure-temperature conditions deviate from their values at phase equilibrium. Our results suggest that the diffusion-controlled mechanism is most likely to operate at the β/γ phase boundary in the mantle, but a martensitic β -to- γ transformation might occur in subduction zones and could reduce the shear strength of the subducting slab.

We performed high-pressure experiments using a 1,000-ton uniaxial split-sphere apparatus^{12,13}. The sample assembly consisted of an MgO octahedron, with an edge length of 10 mm, containing a cylindrical Pt heater^{14,15}. The starting material for the experiments was Mg_2SiO_4 olivine (forsterite) powder which was packed into the full length of the Pt heater. The temperature was measured at the centre of the sample using a Pt-Pt13%Rh thermocouple. Because the ends of the sample were in contact with the tungsten carbide anvils and therefore at relatively low temperature, there was a significant temperature gradient along the axis of the sample.

Experiments were initiated by hot-pressing the forsterite powder in the olivine stability field at 12 GPa and 1,200 °C (at the thermocouple) for 1 h (Fig. 1). Then, by reducing the temperature to 900 °C and further increasing the pressure to 15 GPa, the hot-pressed forsterite was partially transformed to its high-pressure polymorphs in two experiments, for times of 1 h and 5 h. We studied the products of the experiments by transmission electron microscopy (TEM) as well as X-ray diffraction and light optical microscopy¹⁶.

In the 1-h experiment, the forsterite within 300 μm of the thermocouple partially transformed to its high-pressure polymorphs with a grain size $< 1 \mu\text{m}$. Although β -phase was the predominant product, $\sim 10\%$ of the new grains consisted of γ -spinel. The spinel grains contain a high density of faults parallel to [110] which can be easily detected at low magnification in the TEM. High-resolution images (Fig. 2a) show that the faults consist of lamellae of β -phase which typically vary from one to six unit cells in width. The high-resolution images of these β -phase lamellae together with selected-area

Why this reln. - cause even tho have less CFC's have more of further essential element of the rxn. (the heterogeneous surface) - is so, this $\Rightarrow$ that it was the surface that was being reagent.

is not but - is CI melt on start by 2010 - will effects of phase out be felt - that reaching in 2010 TS produce what? what time??

by a factor of 23

A volcanic eruption now could shred the polluted ozone layer

By Jeff Nesmith

Journal-Constitution Washington Bureau

WASHINGTON—Even if the world drastically curtails the use of ozone-destroying chemicals, a large volcano could touch off a catastrophic worldwide ozone loss sometime in the next 20 or 30 years, scientists warned Wednesday.

A volcano similar in size to the 1982 El Chichon eruption in

Mexico would accelerate chemical reactions between ozone and millions of tons of chlorofluorocarbon chemicals that will continue to float in the atmosphere for years after use of the substances has ended, said Guy F. Brasseur, a physicist at the National Center for Atmospheric Research in Boulder, Colo.

In effect, conditions similar to those that cause annual ozone "holes" to appear over Antarctica

could develop over the entire planet, he said.

Within weeks, up to 12 percent of the protective gas would vanish from the stratosphere over populated areas of North America, Europe and Asia.

The calculations assume that 95 percent of the use of chlorofluorocarbons, known as CFCs, would be phased out by the year 2000, as called for under the Montreal Accord, a treaty to end

the use of the ozone-destroying chemicals.

Even with the phaseout, however, conditions have been primed for the complicated interactions among volcanic gas, ozone and chlorofluorocarbons that would remain in the atmosphere for years after emissions stop, Dr. Brasseur said. Therefore, no one can avert the ozone loss that would occur with a large volcanic eruption.

"There is nothing we can do," Dr. Brasseur said. "We can only hope that such a volcano does not occur."

Typically, an eruption the size of El Chichon occurs every few decades.

A loss of 12 percent of the ozone would be about twice as much depletion as scientists have recorded since the discovery that chlorine from CFCs was depleting ozone from the

stratosphere.

In the stratosphere, ozone protects the Earth's surface from ultraviolet radiation from the sun. Additional ultraviolet radiation would increase incidence of skin cancer and damage crops and fisheries, scientists say.

According to some calculations, a loss of 12 percent of the ozone would lead to increases of up to 48 percent in incidence of melanoma.

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Scientific Aspects of the Mt. Pinatubo Eruption and Ozone Depletion

September 24, 1991

Susan Solomon and Daniel L. Albritton,
NOAA Aeronomy Laboratory

1. Ozone-Volcano Connections

Like the polar stratospheric clouds that occur in the Antarctic and Arctic, volcanoes that inject material to the stratosphere can greatly enhance the surface area there. Not all volcanoes can do this - only the unusually forceful eruptions are capable of reaching stratospheric heights. The volcanic surfaces are liquid sulfuric acid/water mixtures, while the polar stratospheric clouds are solid nitric acid/water mixtures. Laboratory studies suggest that some, but not all, of the same surface reactions can take place on the volcanic surfaces as occur on the polar clouds.

The surface area, combined with chlorine chemistry, is believed to lead to ozone depletions. Depletions would likely last for 1-3 years, the time scale required for the stratosphere to 'overturn' and empty out the particles.

A relatively recent large eruption was that of El Chichon, which occurred in Mexico in 1982. An ozone perturbation was noted the following winter and spring at northern mid-latitudes. There is scientific debate concerning whether or not it was caused by the volcanic perturbation.

In addition, some volcanoes inject hydrochloric acid into the stratosphere. This will add to the anthropogenic chlorine already there and represents an additional possible perturbation.

2. Policy Connections

Even in years with little or no volcanic material in the stratosphere, observed ozone losses at mid-latitudes in the northern hemisphere are about 5-10% over the past decade. These are much larger than expected. The mechanism responsible for them must be identified if we are to understand their implications for regulation of halocarbons and predictions for the future state of the stratosphere.

Some studies suggest that present mid-latitude ozone losses are due to chlorine chemistry coupled with the background sulfuric acid/water particles

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that are always present at mid-latitudes. Therefore, a large volcanic enhancement in such particles should produce a temporary and much larger depletion, allowing for an important test of this idea.

3. Current Status of Knowledge About the Magnitude of the Perturbation

The major eruptions of Mt. Pinatubo that deposited material in the stratosphere were on June 15-16. An additional eruption occurred in early September.

Satellite data on SO₂ absorption indicates an injection of sulfur dioxide roughly 2-3 times that of El Chichon. The SO₂ is converted to sulfate aerosols on a time scale of about one month, so the material injected in June should have already been converted to particles. Some satellite observations of particles suggest that the figure of 2-3 times El Chichon may be conservative.

The injection is the largest seen in at least the past 20 years.

4. Where will it go?

The dynamics of the atmosphere will play an important role in determining where it spreads to and how fast. Most of the volcanic cloud is presently confined to tropical regions. Pieces of the cloud have already been seen over Europe and North America. The aerosol surface area observed in Wyoming in late July was about 5 times bigger than the largest perturbations associated with El Chichon. However, these are just small pieces of the main cloud. The spread of the cloud may be expected to be similar to that of El Chichon to a first approximation. This would suggest that the bulk of the cloud will reach northern mid-latitudes in the October-December 1991 timeframe.

5. How much ozone depletion will result?

Assume that the ozone loss observed following El Chichon was due to volcanic perturbations. El Chichon erupted in April, 1982 at a similar latitude to that of Pinatubo. 15-20% local ozone depletions (near 20 km altitude) were noted at mid-latitudes the following winter and spring. Total column changes were about 5-8%.

Hofmann and Solomon explained why the changes were largest at mid-latitudes, not in the tropics where the injection actually occurred. Basically, the heterogeneous chemistry has to compete with normal gas phase photochemistry. It can do that most effectively when gas phase chemistry is slowest - middle to high latitudes in winter/spring.

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An estimate for Pinatubo based on this argument would be:

- 1) Expect little or no ozone loss in the tropics.
- 2) Expect the largest ozone loss in northern hemisphere mid to high latitudes in the winter/spring of 1992, IF the cloud of particles gets that far that fast (and they probably will).
- 3) Expect ozone losses at least twice those obtained following El Chichon for two reasons:
 - a) the chemistry is nonlinear (i.e., more aerosol may be proportionately more effective in chemical processes).
 - b) there is a lot more chlorine now than there was in 1983. In 1983 there was only 2.5 ppbv. Today we have about 3.5.

6. What if the Ozone Loss Doesn't Happen?

If there is little or no observed ozone loss this winter in spite of the large Mt. Pinatubo perturbation, it implies that ideas about reactions on sulfuric acid/water surfaces are incorrect. This would in turn suggest that the ozone losses at mid-latitudes are more likely to be caused by the spreading of polar ozone depletion chemistry. This would mean that polar processes are more important in global ozone losses than previously thought.

9-25-91

Al -

This is the latest on
Mt. Pinatubo from
Don Albritton / Susan
Sloman. Note that
they predict largest ozone
loss over midlatitudes
in winter / spring of 1992.
If large ozone loss does
not occur, this would
imply that ~~the~~ sulfate
theory is incorrect.

Katie.